STUDIES ON SOME AZOMETHINE, PHOSPHORANE AND ARSORANE INTERMEDIATES

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CERTIFICATE

Certified that the thesis entitled, " STUDIES ON SOME AZOMETHINE,PHOSPHORANE and ARSORANE INTERMEDIATES" by Mr. Pankaj Kumar Pathak embodies the work carried out by him under my supervision. Unless otherwise stated, the work reported in the thesis is all original and has not been submitted elsewhere for the award of a degree. Mr. Pathak has worked for more than 200 days attendance in laboratory during this work.

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PANKAJ KUMAR PATHAK

PREFACE

The thesis entitled, "Studies on some azomethine, phosphorane and arsorane intermediates," has been divided into seven chapters and each chapter is equipped with different aspects of ylid intermediate chemistry.

In Chaptr I, a brief survey on ylid intermediates has been described with the special reference to phosphorane, arsorane and azomethine intermediates under seprate heads.

In Chapter II, the elaboration of several semi-stabilized phosphorane intermediates has been carried out by reacting them with 5-phenyl-1,2-dithiole-3-one and 3-thione to give substituted 1,2-dithiafulvenes. This route is rather convenient and facile than conventional methods reported earlier.

In Chapter III author has focussed his studies on the generation and isolation of a new phosphonate carbanion-dimethyl 2,7-dichloro-9-fluorenenylphosphonate carbanion and its reaction with a number of aromatic aldehydes and ketones to synthesize olefins.

Chapter IV describes the useful and excellent results of author's experiments on the effect of bulky size of carbonyl systems of betaine decomposition of semi-stabilized arsorane intermediates.

In Chapter V, author reported the reaction of benzyl arsonium bromide and 4-nitrobenzylarsonium bromide with α,β - un

saturated ketones in presence of anhydrous $AlCl_3$ or $ZnCl_2$ at 150-200 C to give 1,3-diarylnaphthalenes and 1,3-diaryl-7-nitronaphthalenes in fair to good yields.

Chapter VI contains the synthesis of symmetrical and asymmetrical p-substituted phenacylideneazomethine intermediate, generated from their corresponding salts and aromatic aldehydes having electron attracting and repelling effect. This synthesis has been carried out with a view to confirm the course of reaction.

In Chapter VII, author reported the reaction of benzylpyridinium bromide and o-chlorobenzylpyridinium bromide with various substituted benzylidene acetophenones with a view to investigate the applicability of this route in the synthesis of a wide range of naphthalene derivatives.

CHAPTER - I

STUDIES ON SOME PHOSPHORANE, ARSORANE AND AZOMETHINE INTERMEDIATES

A GENERAL SURVEY

The term 'ylid' introduced in synthetic organic chemistry by G.Wittig, is employed for a new and unique class of zwitterionic compounds having remarkable synthetic potentialities. Ylids which have, in general, an anion covalently bonded to a positively charged heteroatom, have gained considerable importance in theoretical and synthetic organic chemistry. They are considered as the resonance hybrids of two canonical structures, the ylid form (Ia) and the ylene form (Ib). Out of these two structures it is the ylid form (Ia) which emphasizes the dipolar zwitterionic nature involving an onium centre at the elements like N, P, As, S, Sb, Bi, Se, Ni, Te etc. next to a carbanionic function which may at least partially be

delocalized into suitable substituents. However, in the ylene form (Ib), a true double bond is postulated between the onium centre and the ylidic carbon, thus reducing or even eliminating the formal charges at these atoms[1,2]

The results obtained by applying modern physical techniques and sophisticated theoretical computation,[3-5] it is made increasingly clear that it is the ylid form that predominates in the ground state. In fact most of the investigations made earlier have sucessfully used the 'ylid' description to solve almost all of their problems regarding structure and reactivity and the rationalization of reaction mechanism.[2,6]

Both, the properties of the carbanion and the involvement of the heteroatom, affect the stability and hence the reactivity of the ylids. The symmetry of the molecule and the magnitude of $p\pi - d\pi$ bonding has made possible the quantitative comparison of the stabilities of ylids of various elements by using the rates of alkali catalysed exchange 7 of α —hydogen atoms of the corresponding salts. It has been established that the acidity of the salt and eventually the stability of ylid is normally affected by any alteration in its structure.

On the basis of stability and the ease with which they undergo chemical reaction with a wide range of electrophilic substrates, ylids may be conveniently classified into two large groups. The first and the larger group comprises of the ylids so called 'non- stabilized ylids' which are generated in the solution from their corresponding salts but could not be

isolated due the lack of stabilizing factors and undergo reactions *in situ*. These ylids may further be sub-divided into two categories depanding on the attachment of alkyl or arylalkyl groups with the heteroatom. The alkylidene ylids are very short-lived but highly reactive, whereas the arylalkylidene ylids oftenly termed as semi-stabilized ylids which though could not be isolated, yet persisted in solution for a considerable period of time.

The second and the smaller group of ylids consists of those designated as 'stabilized ylids' and is taken to imply an ylid which can not be isolated and purified but also in most of the cases stored usually under atmospheric conditions for considerable period of time to be used in subsequent reactions. The unusual extra-stability of these ylids is attributed to the attachment of the electron withdrawing groups with the ylidic carbanion.

The scope and the potential for synthetic applications of these ylids has only been realized recently and studies on these reactive intermediates have been expanded in many directions which led to the exploration of the ylids of nitrogen, phosphorus, arsenic, antimony, bismuth, selenium, sulphur and tellurium as evidenced by the research monographs[1,2,9-12] and comprehensive review articles.[13-37] The involvement of a particular heteroatom results into marked differences in the chemical and physical behaviour of different types of ylids.[1] These investigations have led also to the

synthesis of a wide variety of heterocyclic compounds, natural products, vitamins, harmones etc. as evidenced by a number of publications.[8-37] A brief description under separate heads is given in the following sections.

I. PHOSPHORANE INTERMEDIATES (PHOSPHONIUM YLIDS)

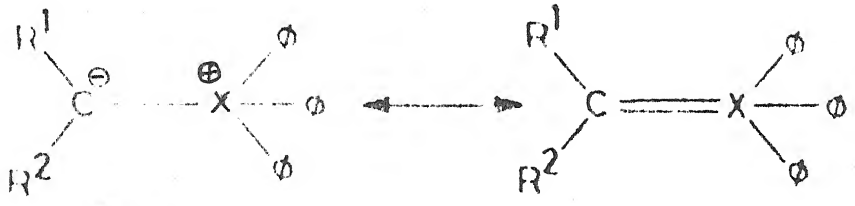
Shortly after world war -II, Wittig directed his attention to the question of the existence of pentavalent nitrogen compounds and discovered in the course of these studies, the nitrogen ylid of the type (6)[38] which was prepared by the action of phenyllithium on tetramethylammonium salt (5). Formation of the Azomethine intermediate (6) was proved by its addition to benzophenone (7) to give (2-hydroxy-2,2-diphenyl) trimethylammonium salt (8) (scheme I.1). Such success clearly required the study of the families of ylids other than those related to nitrogen. Later on, the studies were carried out with next higher element of Vth group, i.e. phosphorus . The declared aim of this work was started in 1953 by the publication with Geissler [39] to be the preparation of stereoisomers of pentaphenylphosphorus as representatives of new class of compounds.This work led to the first synthesis of crystalline methylenetriphenylphosphorane which when reacted with benzophenone surprisingly gave an unexpected new product(10). This reaction signaled the birth of Wittig reaction. In a total six lines of text, Wittig and Geissler described the almost quantitative conversion of methylenetriphenylphosphorane (9) with

benzophenone (7) to give triphenylphosphine oxide and 1,1-diphenylethylene(10) (scheme I.2)

In general, phosphorane intermediates are more stable than azomethine intermediates . Their stability is due to an overlap of the doubly occupied 2p-orbital of the ylid carbon with the unoccupied 3d-orbital of the phosphorus atom and can be represented by the resonance hybrids of two cannonical structures, the ylid form (11 a) and the ylene form (11b) . A similar configuration, however, can not be considered in case of azomethine intermediates. The polarisability effects are more important in phosphorane intermediates as compared to azomethine intermediates but can not counterbalance the difference of Coulombic interaction. In fact, the stability of phosphorane intermediates is due mainly to the possibility of the 3d phosphorus orbital forming actual bonds. [40] This explains the fact that a greater number of phosphorane intermediates have been isolated and characterized as stable species. [41-50] According to Jaffe[51] and Craig et al.,[52] the multiple bonds which involve the overlap of p- and d-orbitals provide the actual chemical stability of these molecules. However, from the ESCA data,[53] it has been established that in the case of phosphorane intermediates with electron withdrawing substituents, the formal negative charge at the ylid carbon is actually highly delocalized on substituents on the ylid of type (2) . The ylid carbon forms an sp^2 orbital with non-bonding doublet in the $2p_z$ (3a) or forms a tetrahedral orbital with phosphorus (3b). The carbanion

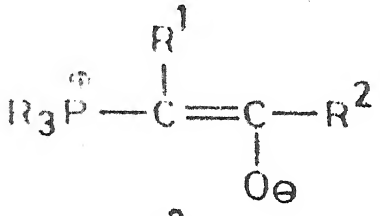
structure is usually sp^2 but some examples are known in which carbon atom is of sp^3 hybridization . The phosphorus atom involved in the ylid fomation is bipyramidally hybridized (dsp^2). [54] The carbon atom can be in an axial position (4a) or at the base of the pyramid (4b). However, an ab initio LCAO-MO-SCF study,[55] made recently of the model ylid, methylenephosphorane shows a planar stereochemistry at the ylidic carbon atom . This results has been rationalized in terms of maximum heteroatom C-π overlap.

The phosphorane intermediates undergo two basic types of reactions those in which only the ylid carbanion is involved mechanistically and those in which both the carbanion and heteroatom portion are involved. The reactivity of alkylidenephosphoranes is determined by the distribution of the negative charge in the molecule which, in turn, depends on the nature of the substituents R^1 and R^2 in the alkylidene portion as well as on the group R on phosphorus. Thus, the nucleophilic character of phosphorane intermediates is decreased and the stability is increased if the lone pair of electrons on the α-carbon atom of form (11a) is delocalized into group R^1 and R^2. The electron withdrawing substituents R^1 and R^2 will stabilize the negative charge and consequently reduce the reactivity of ylid where there is no such interaction, an extremely reactive and unstable ylid is formed. This reaction has since become of general chemical knowledge as the Wittig reaction or Wittig olefination and it influenced the development of synthetic



1a 1 1b

X = N, P, As, S, Sn, Sb, Bi etc



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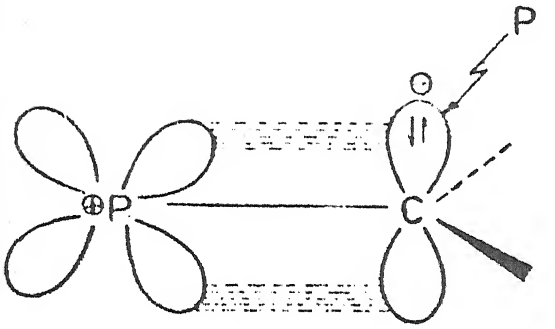
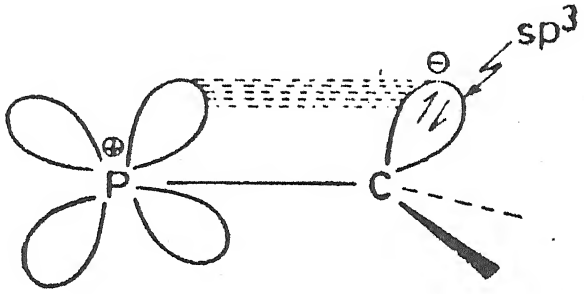


3a



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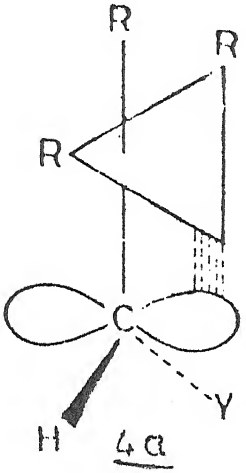
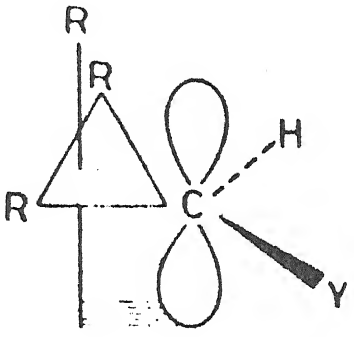


4a



4b

chemistry in the following years to an almost unparallel degree as evidenced by the award of noble prize in 1979 to George Wittig of Heidelberg University. It initiated creative activity in the laboratories throughout the World, as the challenge was taken up to establish the preparative potential of the reaction to study its mechanistic aspects e.g. its stereochemistry or to investigate its effects on neghbouring disciplines.

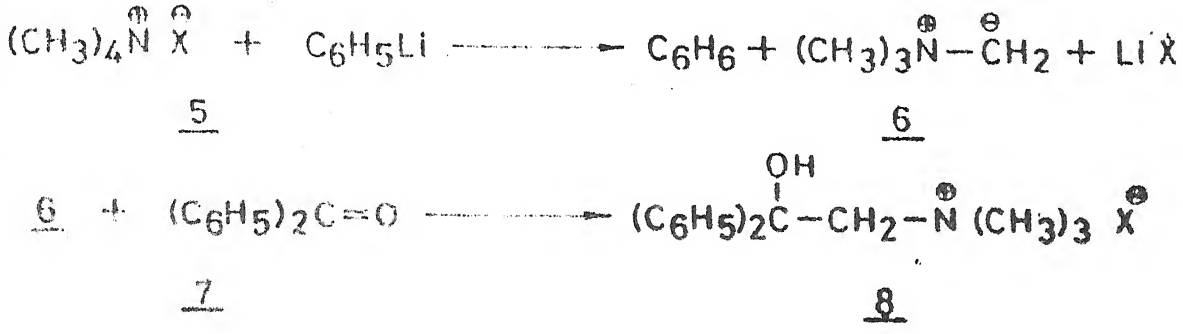
I .A.1 GENERATION OF PHOSPHORANE INTERMEDIATES(PHOSPHONIUM YLIDS)

Following important methods for the generation of phosphorane intermediates have been described :

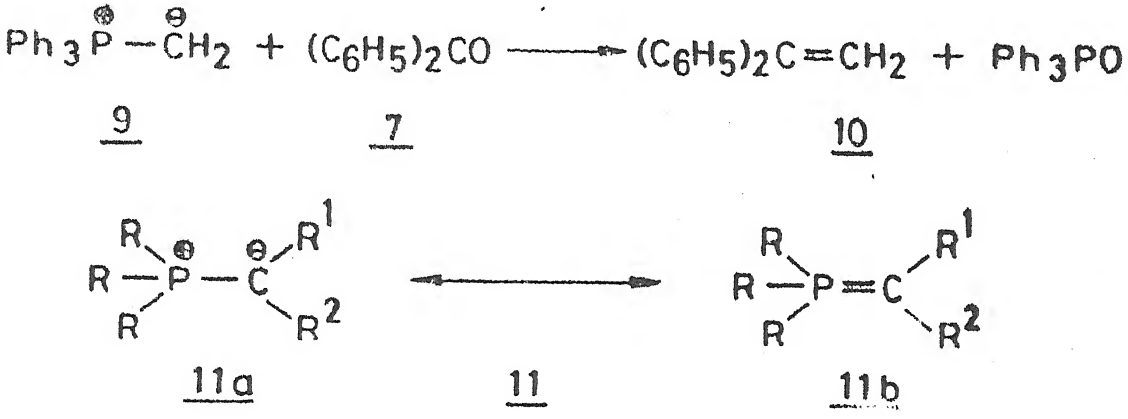
A. 1. 1 Phosphrane Intermemediates from phosphonium salts (salt method)

The most applicable method for the generation of phosphorane intermediates(13) is the action of suitable bases on quanternary phosphonium salts (12) that in turn are obtained from the quaternization of trialkyl or triarylphosphines with alkyl hailides [40,54] (Scheme I.3). The quaternization reaction is usually carried out in a non-polar solvent such as benzenebut sometimes a more polar solvent is also used advantageously. However , it is the acidity of the phosphonium salts and more specifically the nature of substituents R^1 and R^2 on potential ylid carbanion that decides how strong base is needed for the deprotonation of the phosphonium salts to generate the phosphorane intermediates. The base generally used for this

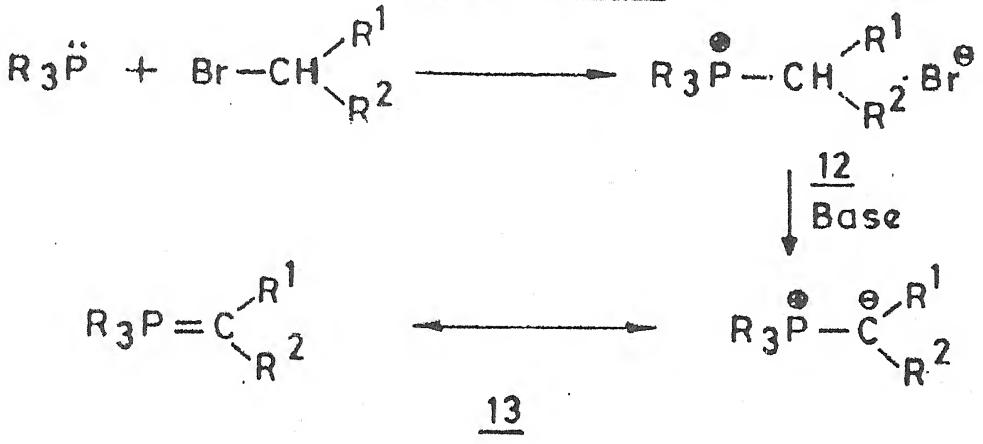
Scheme 1·1



Scheme 1·2



Scheme 1·3



purpose are ammonia,[57] triethylamine, [58, 59] pyridine,[57, 60] sodium hydroxide,[57-61] sodium ethoxide,[62] sodamide,[63] sodium hydride[63], lithium diethylamide,[64] potassium t-butoxide,[65] lithium piperidide,[63] butyl-lithium [66] and phenyllithium.[67]

A.1.2 Phoshorane Intermediate from carbenes and triphenyl phosphine

Phosphorane intermediates are prepared by the interaction of carbon tetrachloride or carbon tetrabromide with triphenylphosphine [68,69](scheme I.4). The diazoliphatics (15) may also serve as a source of carbene for the preparation of phosphorane intermediates(16) provided, they are decomposed in the presence of Cu(I) salt, since triphenylphosphine is generally very much susceptible to diazo compounds to react and form phosphazine(17) [70] (scheme I.5).

A.1.3 Phosphorane Intermediates from phosphine and activated multiple bond

Phosphorane intermediates (18) can also be synthesized by the interaction of triarylphosphine with a compound associated with multiple bonds having electron-withdrawing groups [68,71,72] (scheme I.6).

A.1.4 Phosphorane Intermediate from phosphonium salts by pyrolysis

The thermally less stable phosphonium salt (19) on

pyrolysis yields stable phosphorane intermediates (20) [73] (scheme I.7) .

A.1.5. Phosphorane Intermediates from vinyltriphenylphosphonium salt

The synthesis of phosphorane intermediates(22) is also possible by the action of phenyllithium on vinyltriphenylphosphonium bromide (21) [74](scheme I.8).

A.1.6 Phosphorane Intermediates from the compounds having active methylene group

When dihalotriphenylphosphine (23) is heated with active methylene compounds (24) in presence of tertiary-amine, phosphonrane intermediates (25) is directly formed [75] (scheme I.9).

A. 1. 7 Phosphorane Intermediates from benzyne intermediate

Due to its high reactivity, benzyne intermediate (26) quickly couples with trialkyl or triarylphosphine to give ylid(28). The reaction is supposed to occur via a 1,3-dipolar intermediate (27) which rearranges to afford reactive ylid intermediate (28)[76] (scheme I.10).

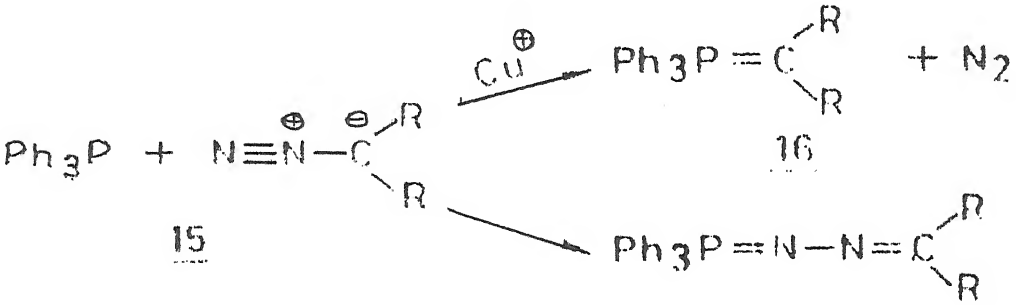
A.1.8 Phosphorane Intermediates from triflates and triarylphosphine

Scheme I·4

14

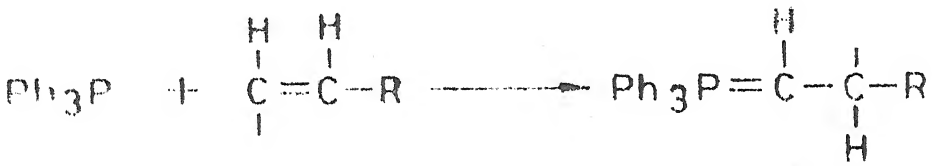
X = Cl, Br

Scheme I·5



15 16 17

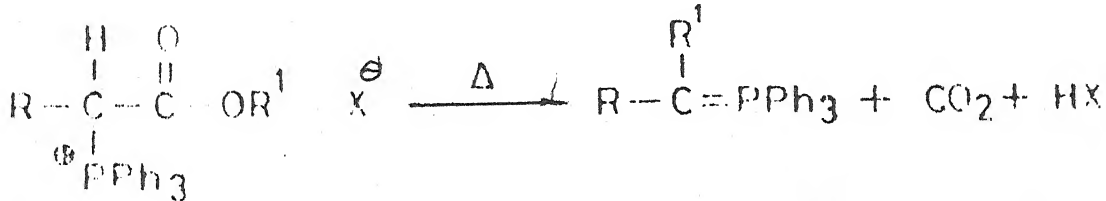
Scheme I·6



18

R = $COOR^1$, $CONH_2$, CN etc.

Scheme I·7



19 20

Recently, syntheses of ylids have been achieved by the reaction of triphenylphosphine and reactive triflats (29) to give phosphonium salts (30), the precursors of phosphorane intermediates, which on treatment with base DBU afford ylid intermediates (31) [77] (scheme I.11)

A. 1. 9 Phosphorane Intermediates via transylidation

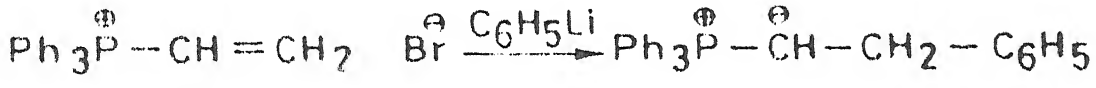
Stable ylids (34) from reactive unstable ylids (32) obtained by thier action with alkyl halides (alkylation)[78] or acyl halides (acylation)[79]. This process is designated as transylidation since 2 molecules of the unstable ylid (32) react with the halide resulting a new carbonyl stabilized ylid (34) (scheme I. 12)

A. 1. 10. Phosphrane Intermediates by other methods

Phosphonium salts, the precursors of phosphorane intermediates have also been prepeared by the reaction of $Ph_3P{=}CHSiMe_3$ with carbonyl compounds,[80] 2-chloro-oxiranes with triphenylphosphine [81],fluorinated α —oxides with trialkyl phosphites [82] and phosphorus trichloride with 3,3-dimethoxyprop-1-ene [83]. Cathodic reduction of phosphonium salts also yields phosphorane intermediates[84].Mixed valance phosphorus germanium ylids have also been prepared from germanium tetrahalide[85].

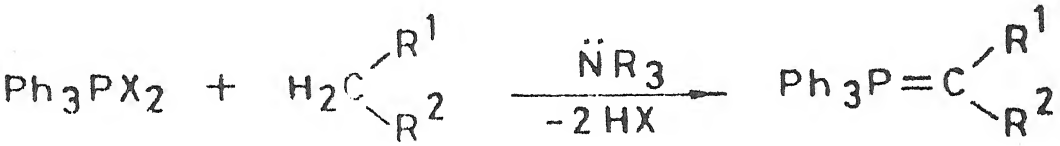
I. A. 2. REACTIVITY OF PHOSPHORANE INTERMEDIATES

Scheme I·8



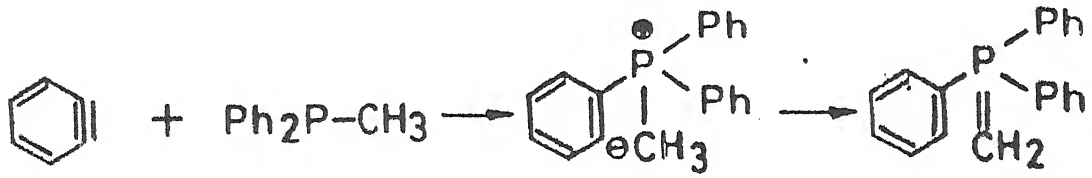
21 22

Scheme I·9



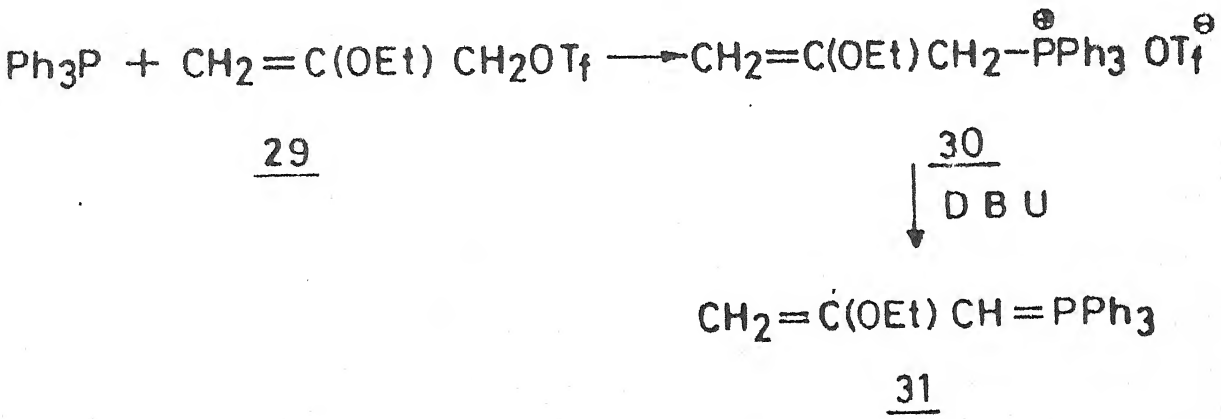
23 24 25

Scheme I·10



26 27 28

Scheme I·11



Ylids as defined earlier, are the unique forms of carbanion and undergo reaction with a wide variety of electrophilic reagents . The unique behaviour of ylid carbaonion is due to the ability of phosphorane intermediates to become pentavalent. This is why ylid carbanions exhibit some typical reactions which are not expected from simple carbanion.

Some interesting and useful reactions of phosphorane intermediates have been illustrated in the following categories:

A.2.1 Phosphorane Intermediates and phosphonium salts as bronsted acid-base pair

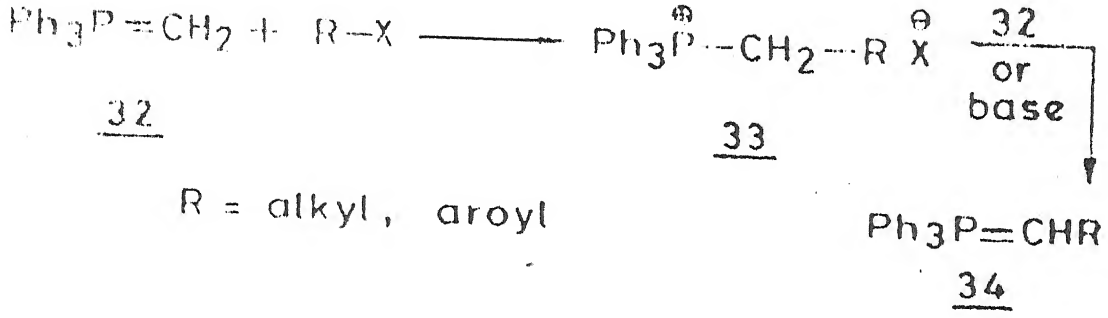
Phosphorane intermediates from their precursors, phosphonium salts by dehydrohalogenation, are able to be attacked by hydrogen halide whereby original salt is regenerated . Therefore, phosphonium salts may be considered as Bronsted acids and the phosphorane intermediate as Bronsted base (scheme I.13).

A. 2. 2 Oxidation of phosphorane intermediates

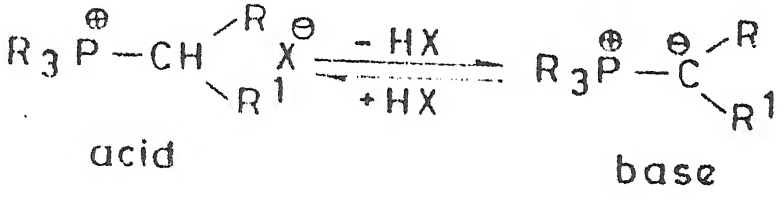
Action of oxygen on phosphorane intermediate (35) involves the cleavage of carbon phosphorus bond yielding a carbonyl compound (36), which further reacts with excess of starting ylid (35) to give an olefin (37) and phosphine oxide [86,87] (scheme I.14).

The autooxidation reactions have also been applied to bis-ylids (38 &40) resulting in the formation of cyclic olefins, acenaphthenes (39) (scheme I.15) and heterocyclic olefins(14)[88]

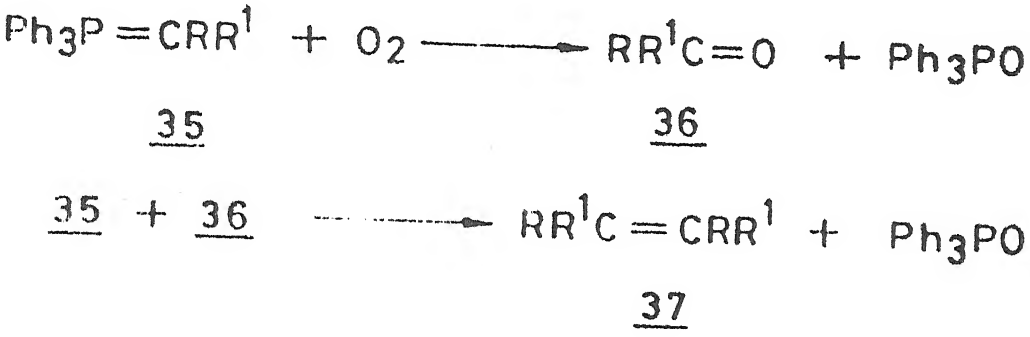
Scheme 1·12



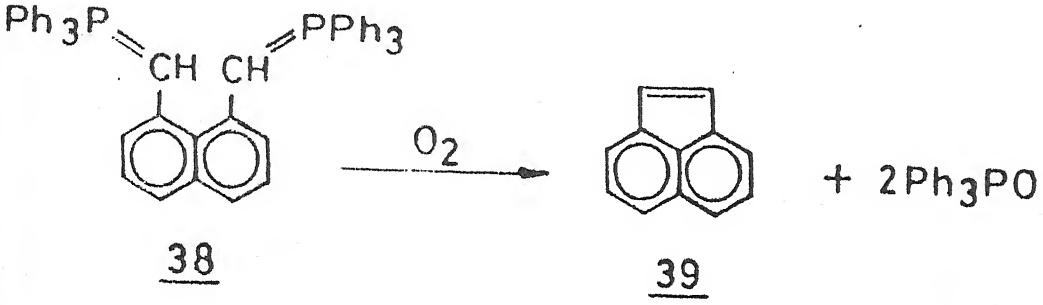
Scheme 1·13



Scheme 1·14



Scheme 1·15



(scheme I.16)

The oxidising agents used in the oxidation of ylid intermediates are ethyl nitrate[89], lead tetrachloride, dibenzoyl peroxide, phenyl iodide diacetate and lead dioxide [90]. The oxidation with ozone [91] and periodate [92] was found to be particularly useful in the synthesis of dicarboxyl compounds .

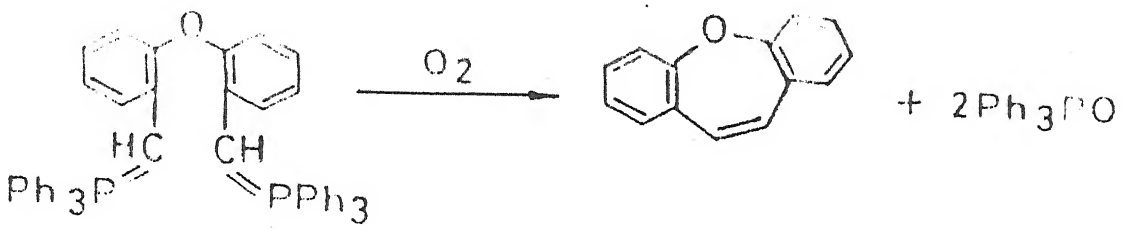
A. 2. 3 Transylidation

Phosphorane intermediates (42) on alkylation with alkyl halide forms phosphonium salts(43) which on further treatment with base or another molecule of the starting phosphonium intermediate (42) gave alkylated ylid intermediate (44)[78] and precursors (45) of ylid intermediate(42) (scheme I.17). On the other hand, carbonyl stabilized ylid intermediates (46), on reaction with alkyl halide form C-alkylated product (47) and O-alkylated product (48) because of the mesomeric forms of ylid intermediate (46) [79] (scheme I.18)

If the ylid intermediate contains a halogen in the long chain attached to carbanion portion, intramolecular alkylation may occur to yield cyclic products (49) [93,94] (scheme I.19)

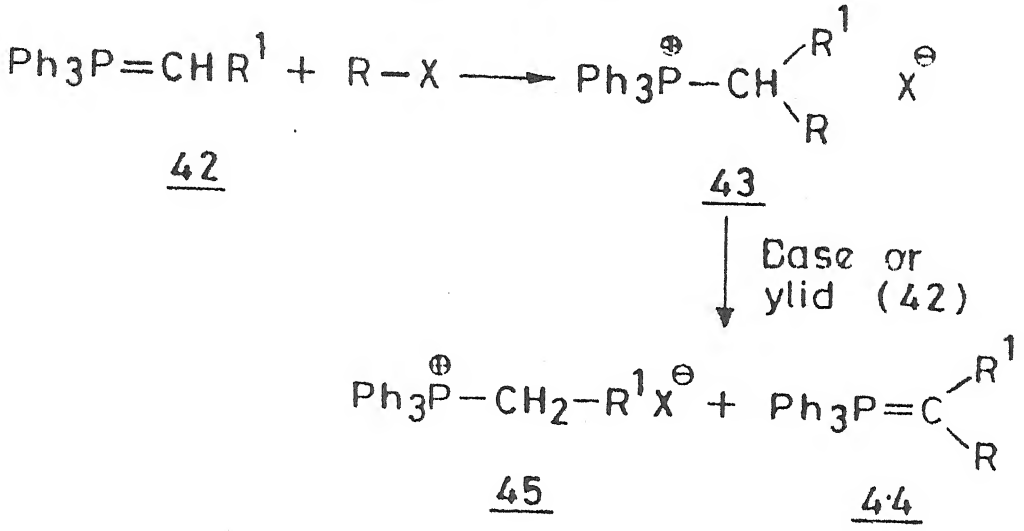
The acylation of ylid intermediate (50) with acid chloride yields an acylated phosphonium salt (51) which on treatment with base or another molecule of ylid intermediate (50) affordsa carbonyl stabilized ylid intermediate (52)[95] (scheme I.20). Acid esters [59,96], chloroformic acid ester [95], acid anhydride[97], thiocarbonic acid and s-ethyl esters[98] may also be used as

Scheme 1·16



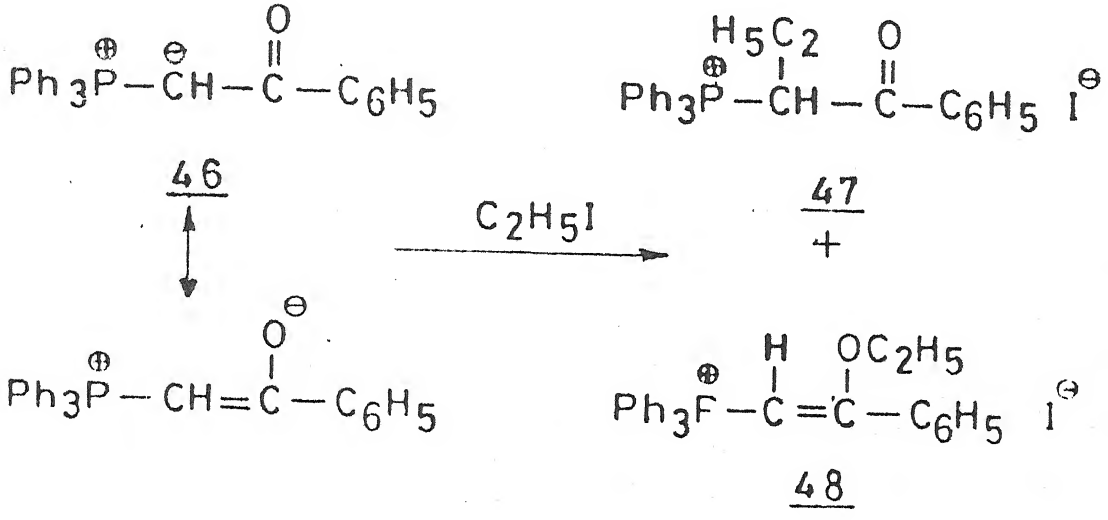
40 41

Scheme 1·17



42 43 45 44

Scheme 1·18



46 47 48

acylating agent.

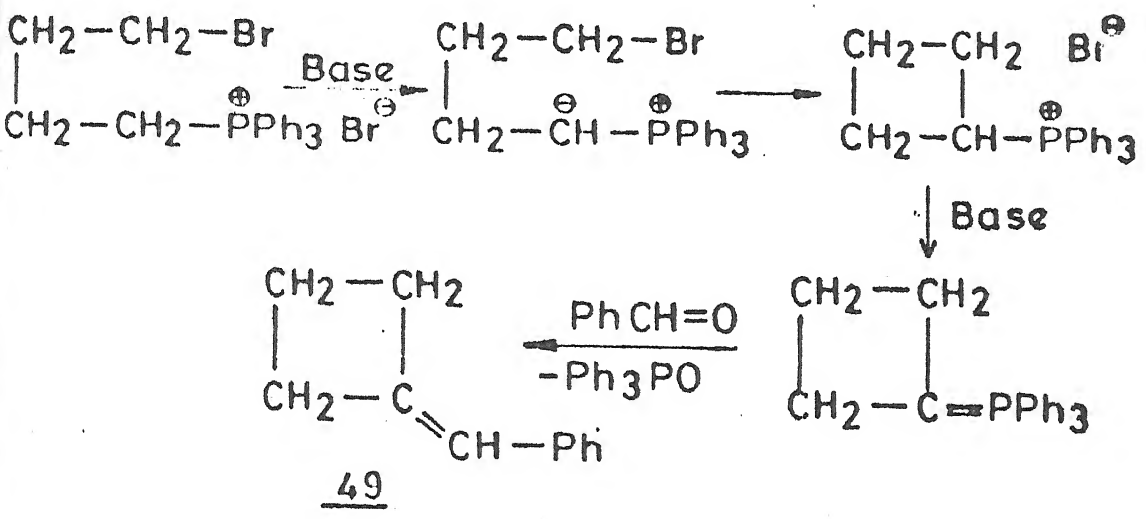
The benzoylation of semi-stabilized phosphorane intermediates to yield highly stabilized ylid intermediates, a transylidation reaction has also been studied by Tewari et al.[98]. Recently Yoshida et al.[99] have reprted the reaction of ylid intermediate (53) with imidoyl chloride (54) to form α-iminophosphoniummethylids (55) as a transylidation reaction (scheme I.21) . Recently, it has also been observed that β-ketophosphoraenes yielded o-acylated product on acylation with acid chlorides [100].

A. 2. 4 Reactions of phosphorane intermediates with multiple bonds

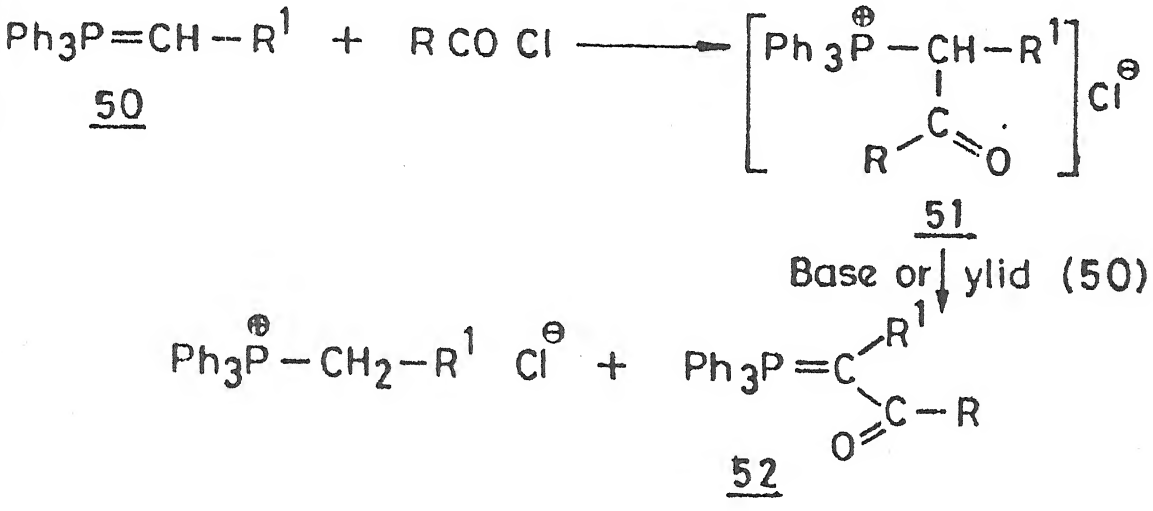
A. 2. 4. 1 Reaction with c=o bond (wittig reaction)

The most versatile reaction of phosphorane intermediate, which attained considerable importance in the synthetic organic chemistry under the name of Wittig reaction, involves the condensation of these ylid intermediates with carbonyl compounds to form olefins and triphenylephosphine oxide [6,91,135-137]. It appeares that during the course of the reaction, betaine type of compounds are formed as intermediates (58). These intermediates (58) are formed by the nucleuophilic attack of ylidic carbanion (56) on the carbonyl group (57) and their decomposition through a cyclic transition state (58 b) yields olefins (59) and phosphine oxide [6,101-103] (scheme I.22) . Thus

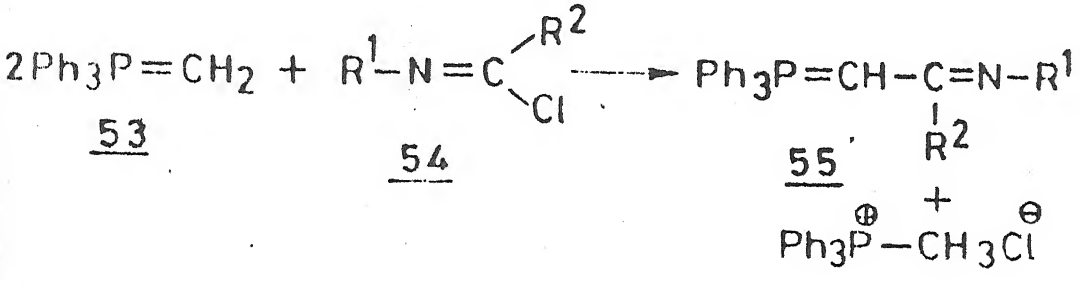
Scheme 1·19



Scheme 1·20



Scheme 1·21



the reaction is a two step process and either of the two steps i.e. (a) betaine formation and (b) its decomposition may be the rate determinig step.

Mechanism of Wittig reaction

(a) Betaine formation

The nucleophilic addition of alkylidenephosphorane in its ylid intermediate form to a polarised carbonyl compound involves the betaine formation (58 b) . As a consequence of the greater affinity of phosphorane for oxygen and tendency of phosphorus atom to expand its valence shell up to 10 electrons, P-O bond is formed giving rise to the four membered ring compound (58 b) .

The nature of substituents R^1 and R^2 in the carbanion portion as well as of the group R on phosphorus determine the ease with which the betaine intermediate is formed .It has been observed that electron-withdrawing nature of group R increases the d-orbital resonance and thereby favours ylene form, thus decreasing the reactivity of the ylid intermediate . If on the other hand, group R has electron releasing substituents, the magnitude of formal charge on phosphorus atom decreases to make greater contribution towards the ylid form. Consequently the reactivity of ylid is increased.[1, 8, 12] The electron withdrawing nature of the group R^1 and R^2 on carbanion side stabilizes the negative charge and consequently nucleophilic character of the ylid is diminished . Conversely, the electron releasing nature of $R^1$and R^2 increases the nucleophilicity of the ylid intermediate .

(b) Betaine decomposition :

The decomposition of the betaine into olefin (59) and phosphine oxide proceeds on the attack of the oxyanion on the phosphoniun atom forming four membered ylidic betain (58 b). [104] The driving force for the decomposition of betaine is derived from the formation of P-O bond because of greater affinity of tertiary phosphine for oxygen . This step will be retarded by substituent R which decreases the positive character and hence oxygen affinity of the phosphine (+I,+M or hyperconjugative effect) and accelerated by the substituent R^1 and R^2 which can conjugate with incipient double bond in transition state . This clearly indicates that the factors which help betaine formation hinder betaine decomposition and vice versa .[102,105,104]

Stereochemistry of Wittig reaction

In a majority of cases Wittig reaction appears to yield trans-olefins as the dominant product [29,30,107-110]. Recently investigations have, however, revealed[111] that normally the carbonyl olefination (Wittig reaction) is not stereoselective and both the isomers are obtained in comparable amounts . Only in some instances, predominant formation of cis- or trans- olefins has been reported . Even such cases give rise to questionable mechanistic interpretations. The stimulated research in this area which lead to the achievement of steric control of the olefin synthesis .

On the basis of the mechanism discussed above, if ylid intermediate and carbonyl compounds are unsymmetrically substituted, a mixture of cis-and- trans- olefins is formed . The ratio of the two forms appears to be governed by a combination of steric factors and reaction conditions .[1,2,12,112]

A phosphorane intermediate may also react with a carbonyl compound to yield a betaine with either the erythro (60) or threo- configuration (61) (scheme I.23)

As the sterically less hindered betaine has threo- configuration, it is expected that trans- isomer being thermodynamically more stable, would predominate . It has been stated that there is no direct conversion of one betaine into other but only through reversion to the starting ylid intermediate and carbonyl compound .[112] However, in the presence of phenyllithium, the interconversion of the betaines(60 & 61) is extremely rapid with the equilibrium as shown in scheme I.23.

Addition of hydrochloric acid followed by the potassium tertiary butoxide gives pure trans-olefins .[114] In a non -polar solvent, the trans- isomer is the predominant product. However, as the polarity of the solvent is increased the yield of cis- olefins also increases.

The presence of an excess of either reactant or addition of nucleophiles and salts such as lithium iodide tends to increase the proportion of cis- form .[112] Thus, by proper control of reaction conditions, carbonyl olefination can be made steroselective to yield a particular isomer, thereby making

Wittig reaction a useful tool in the hands of synthetic organic chemists. Thus the stereoselective olefination of carbonyl compounds has been applied in the preparation of naturally occuring fatty acids.[112] Structural factors and reaction conditions which influence the rate of formation and decomposition of betaines (60 & 61) respectively, thus, determine the steric course of Wittig reaction .[115-117] For this reason, resonance stabilized and non-stabilized or so called moderated ylids are different with regard to their stereochemistry in Wittig reaction.

In addition to the influence of the substituents on the stereochemical course of Wittig reaction, a number of other factors i.e. solvents [116], inorganic halides, [118] acid catalysts, [119] reactant ratio,[116] reaction time [116] and temperature[120] are also important in determing the rate and sterochemical course of reaction.

Recently, D.W.Allen and H.Ward (1980)[121] studied the chemistry of heteroarylphosphonium compounds with a view to investigate the effects of heteroaryl substituents at phosphorus on steric course of Wittig reactions of semi-stabilized and stabilized ylids and reported that the cis- trans- ratio of the stilbenes formed in Wittig reactions of semi-stabilized ylids drived from benzyltri(hetero)arylphosphonium salts in ethanolic ethoxide with benzaldehyde decreases markedly in the series ; 2-furyl > 2-thienyl >phenyl > 1- methylpyrrole-2-yl.

The 2-furyl group favours a greater proportion of the

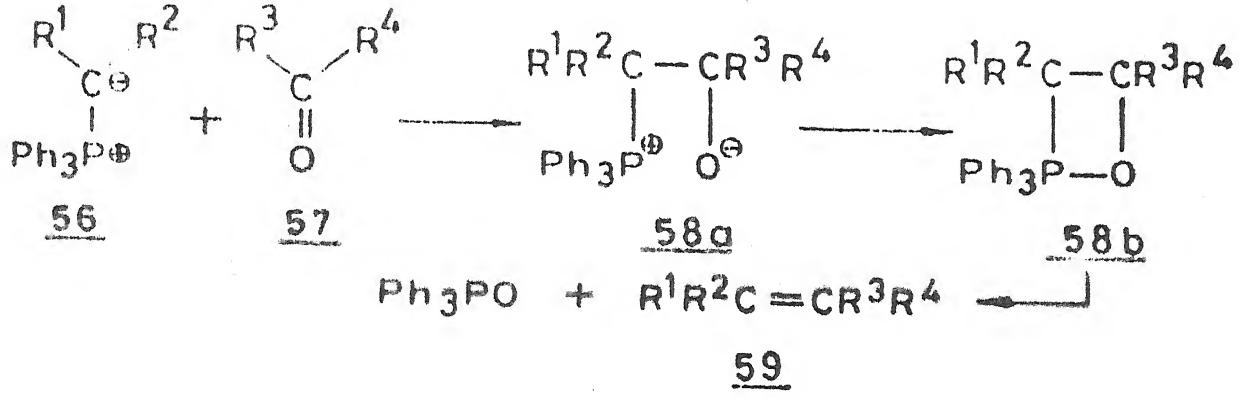
cis-isomer than m-trifluoromethylphenyl where as the 1-methylpyrrole-2-yl group favours a greater proportion of the trans-isomer than p-methoxyphenyl. Similarly, in Wittig reactions of carbonyl stabilized ylids with benzaldehyde and acetaldehyde,the presence of 2-furyl groups at phosphorus results in a significant increase in the proportion of the cis-alkene compared to that formed from the related triphenylphosphorane intermediate .

Applications of Wittig Reaction

Wittig reaction involving condensation of phosphorane intermediate with carbonyl compounds to yield olefins and phosphine oxide has gained big importance because of its mild reaction condition and good yields of products . The possibility of stereoselective carbonyl olefination to yield the derived isomer has made it a particularly useful reaction involving a variety of synthesis.

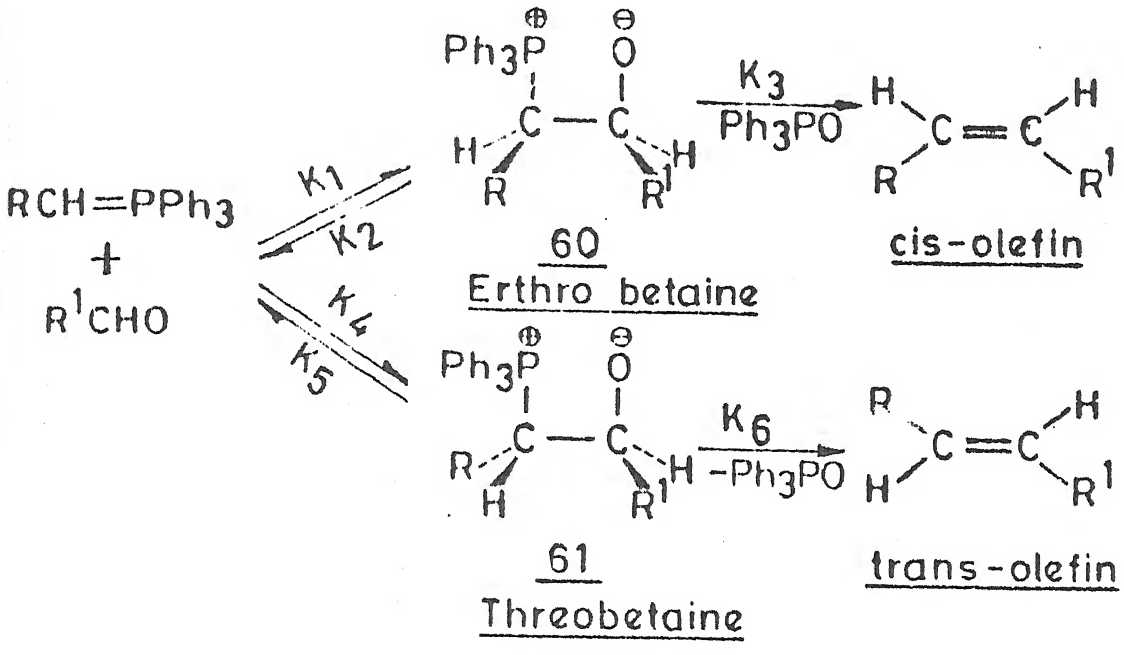
Thus, phosphorane intermediates have been used in the synthesis of a wide range of natural products such as terpenoids-phytone, [122] β-bisabolene[123] and lanceol[124] (scheme I.24). Synthesis of a number of plant pigments such as β-carotene[125] and lycopene[126] has also been carried out . It has also been found useful in the preparation of Vitamins A [127], and D.[128] The extension of sugar chain in carbohydrate chemistry[129-131] (scheme I. 25) has also been brought about by using the reaction . In the recent times, this reaction has been adopted in the synthesis of

Scheme 1·22



56 57 58a 58b 59

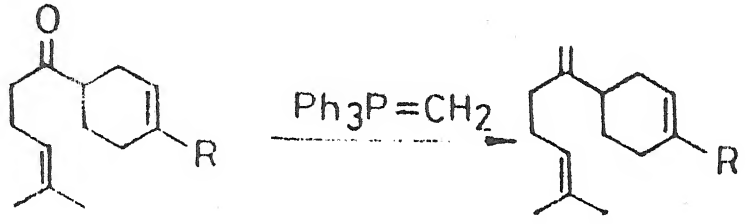
Scheme 1·23



60 Erthro betaine

61 Threobetaine

Scheme 1·24



R = CH_3 (±) Bisabolene

R = $-CH_2OH$ (±) Lanceol

11-deoxyprostaglandins [132] (scheme I.26), macrocyclic [133] (scheme I.27) and the heterocyclic compounds[134] (scheme I.28).

A. 2. 4.2 Reaction with N=O group

Like the carbonyl group, nitroso compounds(63) also undergo Wittig reaction with phosphorane intermediates (62) to form C-N double bond systems (64) which further react with a second molecule of the ylid (62) to give an olefin (65) and iminophosphoranes (66)[135] (scheme I.29).

A. 2. 4. 3 Reaction with C=N group

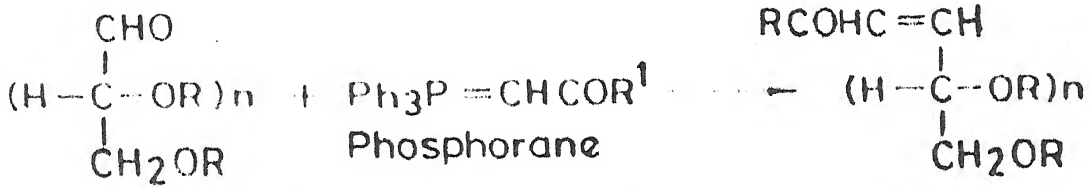
It has been reported by Bestmann and Seng [136] that the ylid (67)which lack β -CH_2 group react with Schiff's bases (68) to give olefins(69) and iminophosphoranes (70) (scheme I.30a) while the ylids with β -CH_2 group undergoes a different reaction with benzalaniline (72) to give allenes (74) forming betaine intermediates (73) in the course of the reaction (scheme I.30).

A.2. 4. 4 Reaction with C≡N group

Benzylidene triphenylphosphorane (75) reacts with benzonitrile (76) to give iminophosphorane (78) via the intermediacy of cyclic product (77).[139] The hydrolysis of cyclic product (77) yields ketones (79)[140] (scheme I.31).

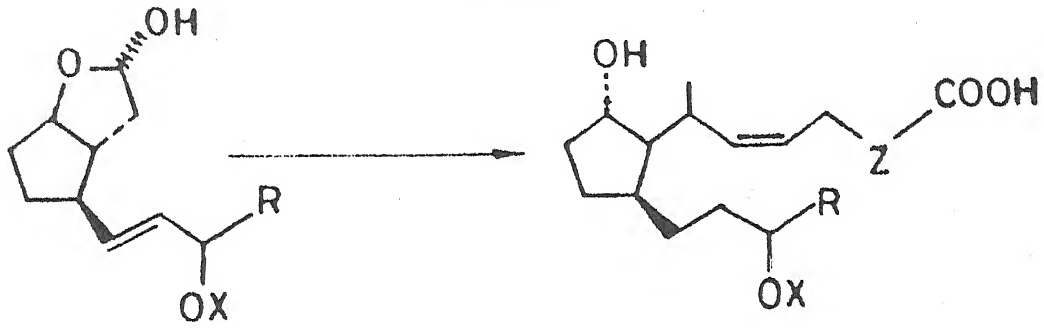
A. 2. 4. 5 Reaction with C≡C bond

Scheme 1·25

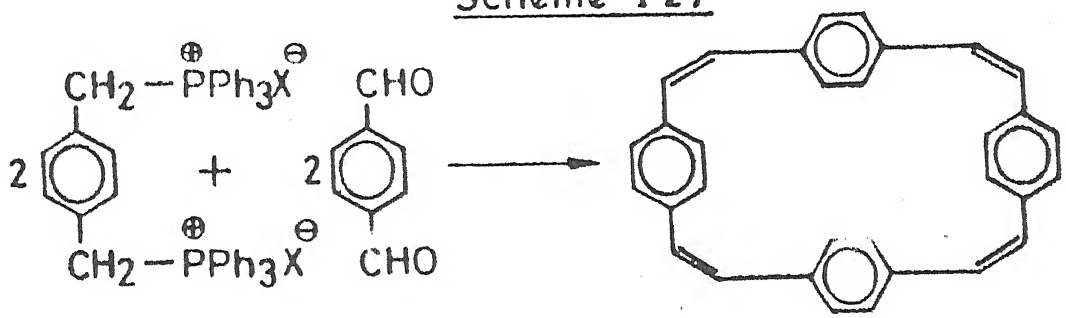


Protected or unprotected aldehydo sugars

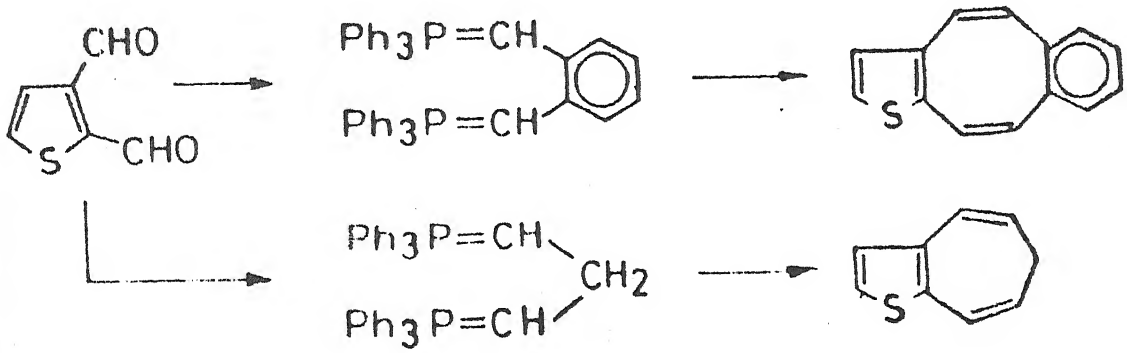
Scheme 1·26



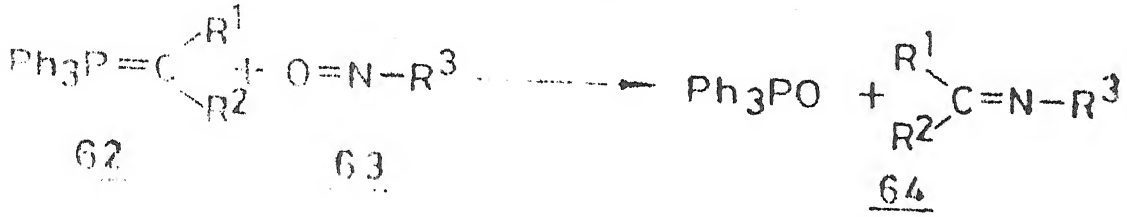
Scheme 1·27



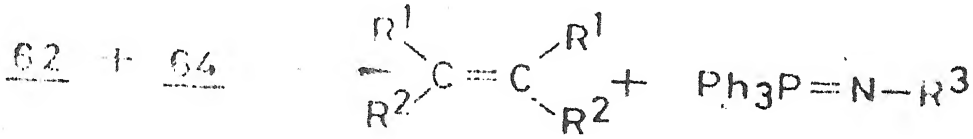
Scheme 1·28



Scheme 1·29

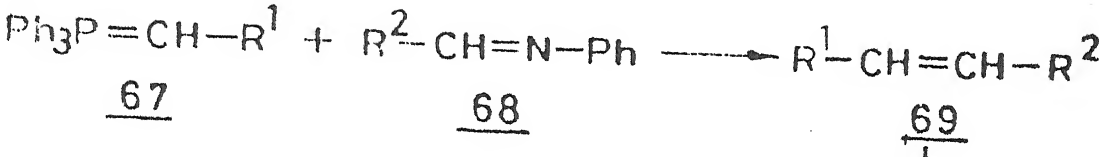


62 63 64



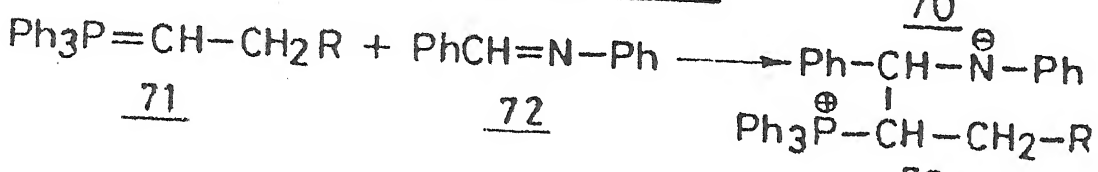
65 66

Scheme 1·30a



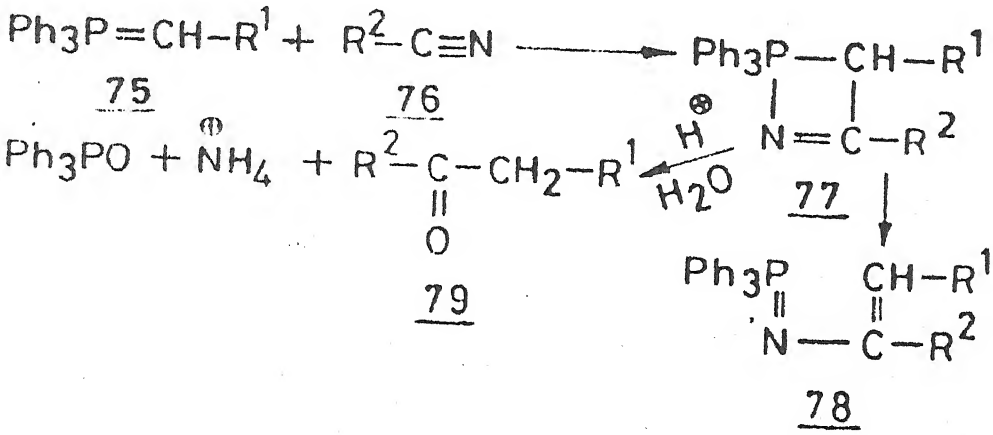
67 68 69 70

Scheme 1.30b



71 72 73 74

Scheme 1·31



75 76 77 78 79

The phosphorane intermediate (80) with acetylene dicarboxylic acid esters (81) lead either through betaine formation (82) or through direct cycloaddition to the phosphacyclobutene (83)which undergoes ring opening to give a more stable phosphorane (84)[141](scheme I.32).

A.2.4.6 Reaction of phosphorane intermediates with 1,3-dipolar compounds

4.6.1 Reaction with azides:

Phenyl azides (85) reacts with benzylidene triphenylphosphorane (86) to yield benzalaniline (87) and N-phenyl triphenylphosphinimine (88) [142] (scheme I.33).

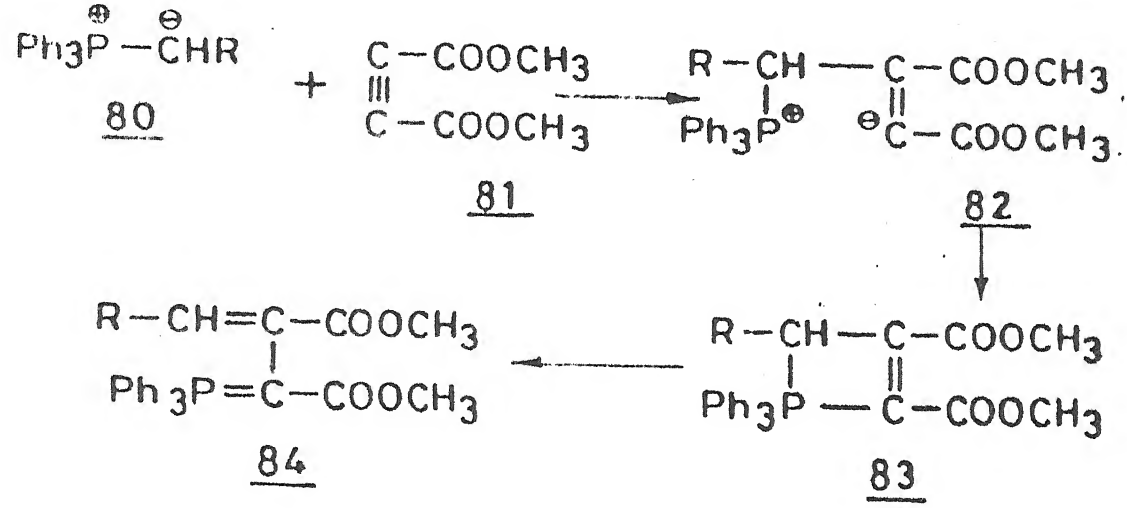
Long chain azides having C=O in chain underwent an intramolecular aza Wittig reaction on treatment with triphenylphosphine in anhydrous diethyl ether under nitrogen to give 60-92 % cyclic imines .[143]

4. 6. 2 Reaction with nitrones

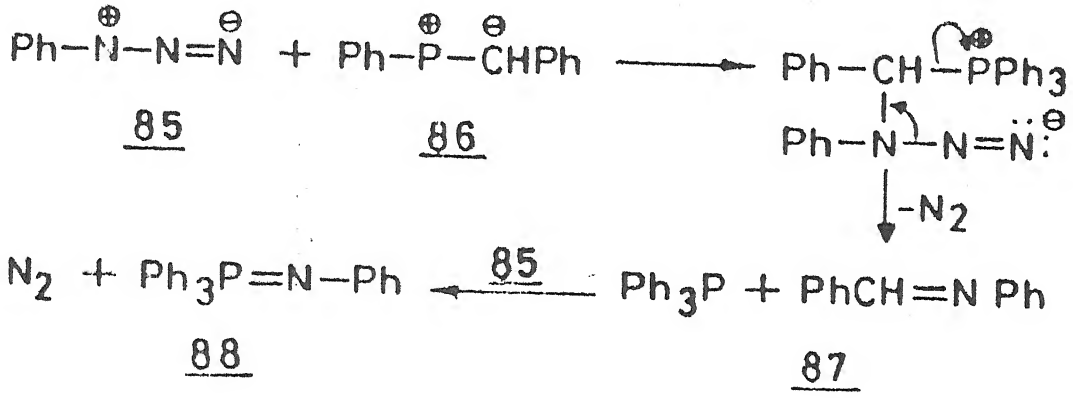
It has been reported by Huisgen et al.[144] that phosphorane intermediate (90) adds to nitrones (89) to give new heterocyclic system i.e. 1,2,5-P(V)-oxazaphospholidines(91) (scheme I.34). It has been suggested that the addition at multiple centre is one step process[145].

4. 6. 3 Reaction with nitrile oxides

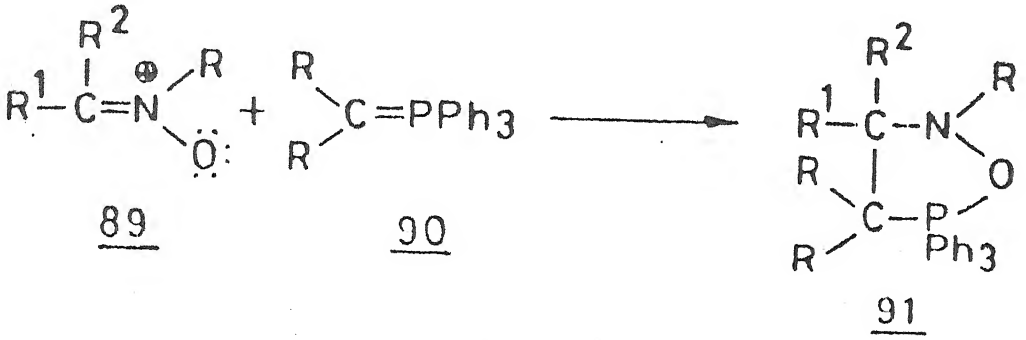
Scheme 1·32



Scheme 1·33



Scheme 1·34



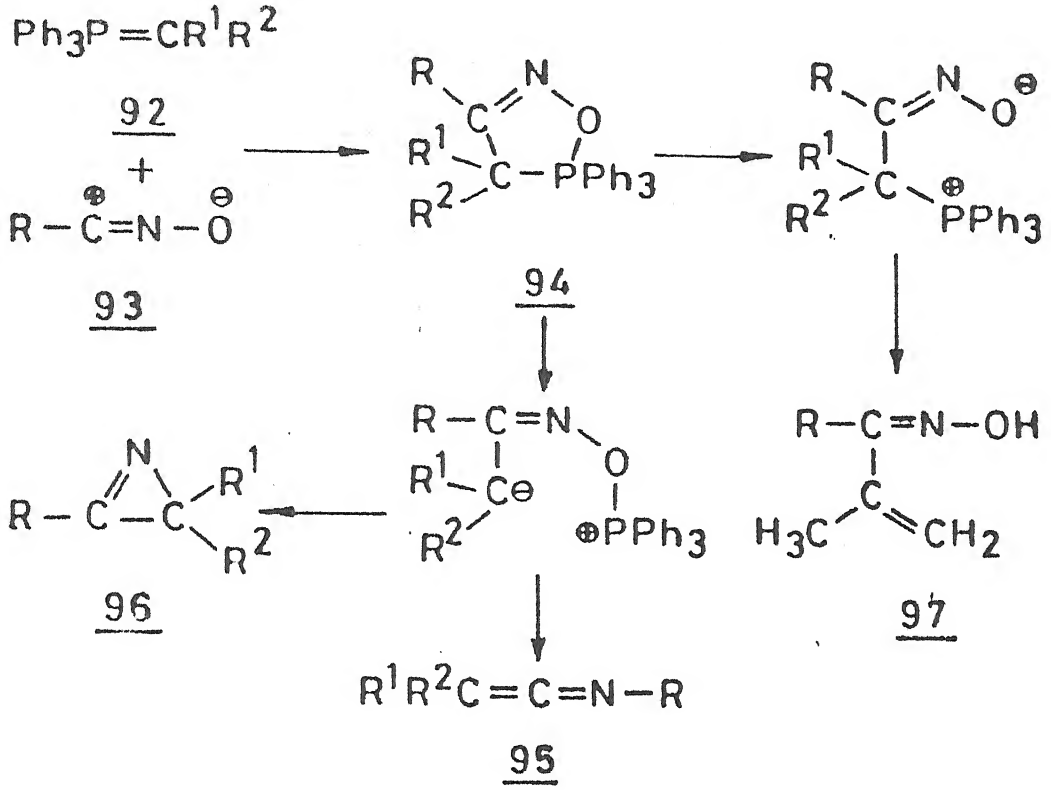
Phoshorane intermediates (92) and nitrile oxides (93) interact to give 4,5-dihydro-1,2,5-P(V)-oxazaphosphlenes (94) whose thermal decomposition yields different products depending upon the nature of substituents [146,147] R,R^1,R^2 (scheme I.35). Thus, the groups R^1 and R^2 when associated with -I and -M effects cause the formation of keteneimines (95) while the same groups which possessed electron-donating tendency affect the formation of azirines (96) . When R exhibits -I effect and at the same R^1 and R^2 show +I effect, the products are triphenylphosphine and α,β —unsaturated oxime (97).[146]

A. 2. 4. 7 Reaction of phosphorane intermediates with esters

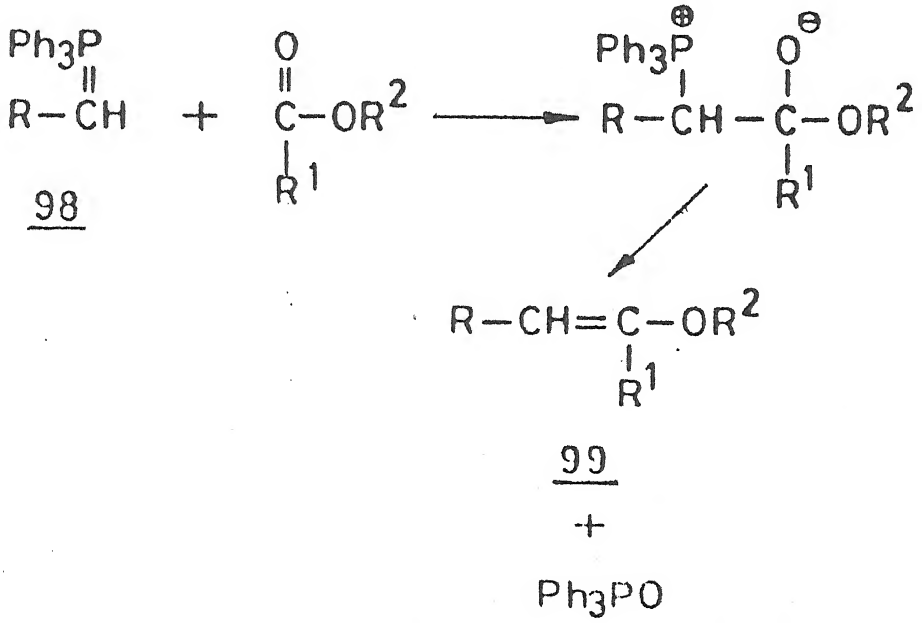
Recently, Subramanyam et al.[148] have studied that the reaction of phosphorane intermediates (98) with ethyl formate gave substituted vinyl ethers(99) via the course of Wittig reaction (scheme I.36) instead of aldehydes as repoted by Trippett et al. [149]. On the other hand, α-iodo or α-bromoacetic acid esters (100) form phosphonium salts (101) using ylid intermediates (98) from which, by transylidation reaction, a new ylid intermediate (102) is produced[150] (scheme I. 37). However, mono-,di- and trifluoroacetic acid esters (103) and phosphorane intermediae (104) undergo Wittig reaction at the ester carbonyl group which results in the formation of enol-ethers (105) of fluoroketones[150] (scheme I.38).

A. 2. 4. 8 Reaction of phosphorane intermediates with lactones

Scheme 1·35



Scheme 1·36



β-propiolactone (106) and γ-butyrolactone (107) with alkylidenetriphenylphosphoranes (108) yield phosphino carboxylate betaine (109), thermolysis of which give triphenylphosphine and lactones (110) with the alkylidene group of the starting phosphranes (108) introduced in the ring [151] (scheme I.39).

On the other hand, enol-lactone (111) with stabilized ylid intermediates (112) give normal Wittig products (113 & 114) (scheme I.40)

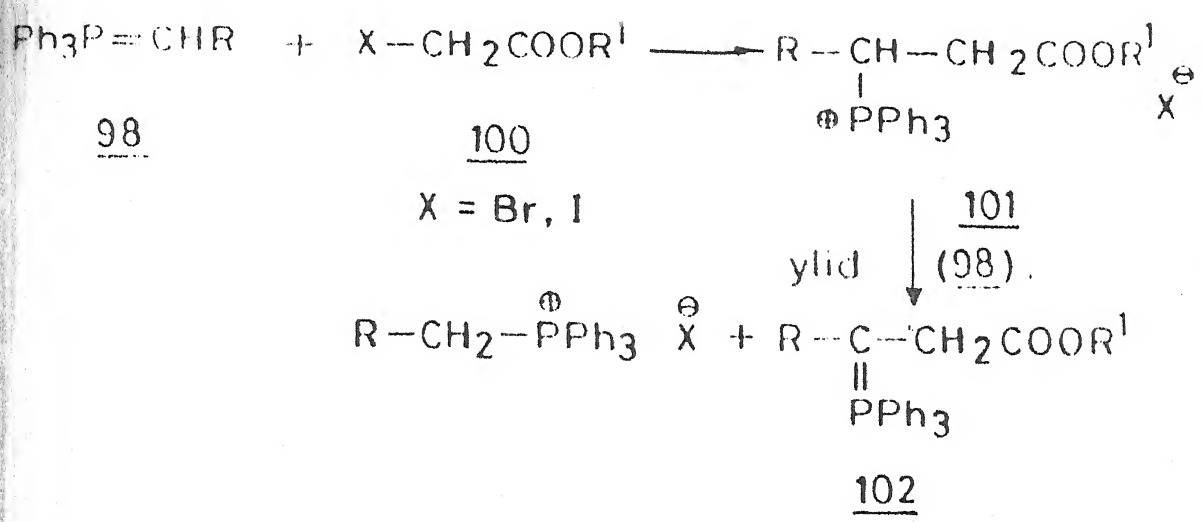
A. 2. 4. 9 Reaction with cyanohydrine

When phosphorane intermediate (115) is reacted with substituted benzaldehyde cyanohydrine (116) in the presence of sodium butoxide to form stilbenes (117a-b) having E,Z conformations. The course of reaction is analogous to Wittig reaction [153] (scheme I.41).

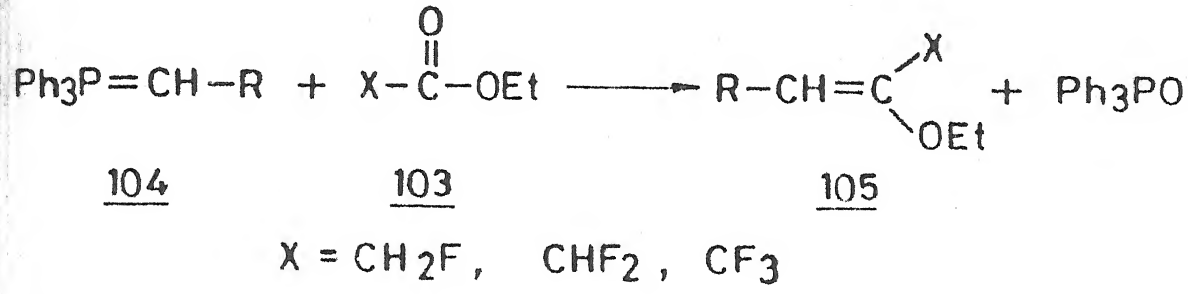
A. 2. 4. 10 Reaction with chalcones

The course of reaction of phosphorane intermediates with carbonyl systems is quite different to that of analogous to azomethine intermediates. But the reaction of phosphorane intermediates (118) with α, β —unsaturated ketones (119) so called chalcones in presence of ammonium acetate undergoes aza-ring closure leading to the synthesis of 2,4,6-triarylpyridines (120)[154] analogous to the azomethine[155-158], sulfurane [159] and arsorane intermediates [160] (scheme I.42) .

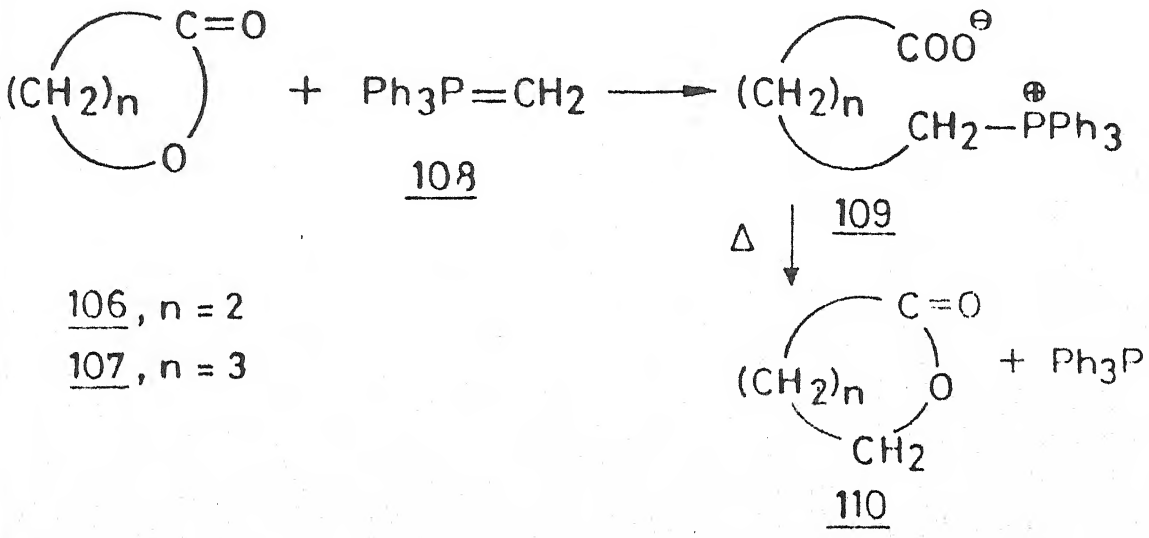
Scheme I·37



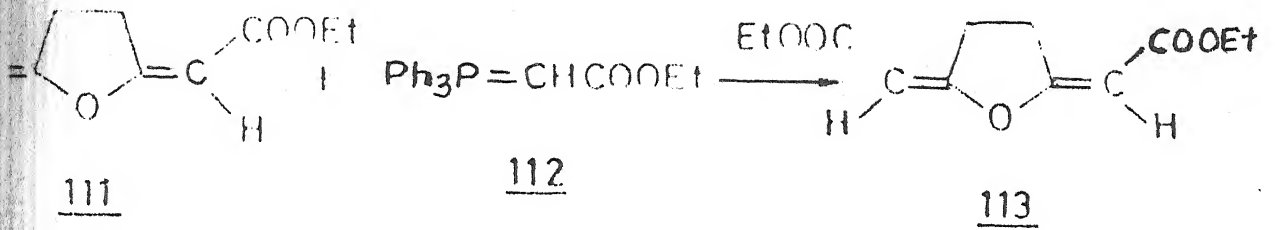
Scheme I·38



Scheme I·39

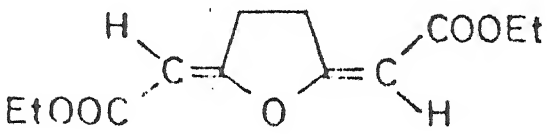


Scheme 1·40



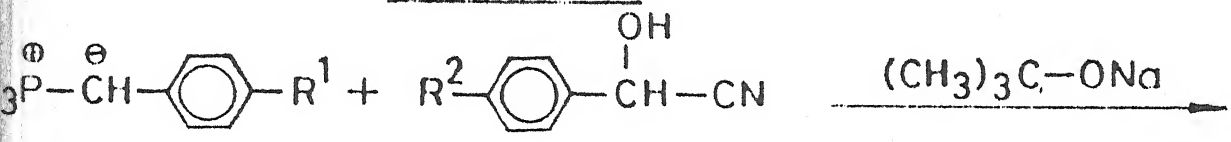
111 112 113

+

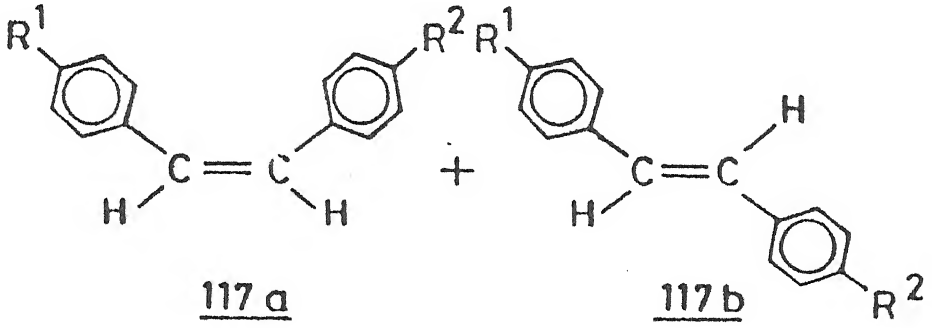


114

Scheme 1·41

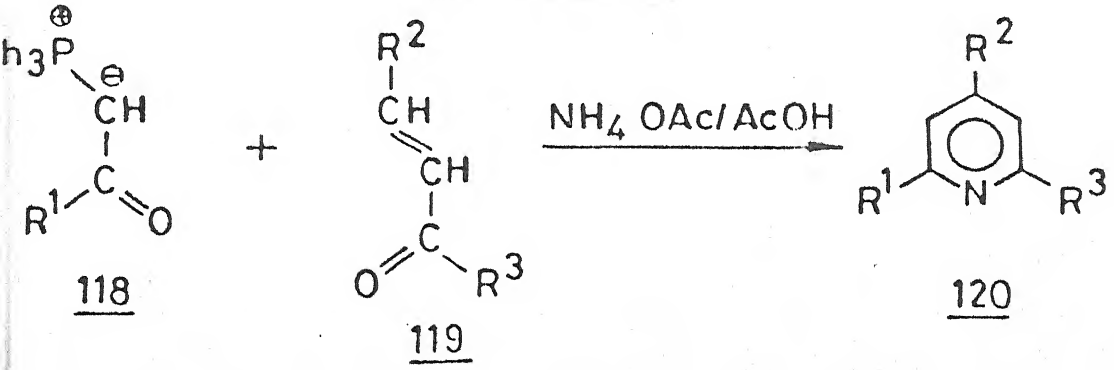


115 116



117a 117b

Scheme 1·42



118 119 120

A. 2. 4. 11 Reaction with N-sulfinylamine

The reaction of stable phosphorane intermediates with N-sulfinylamines give different products depending upon the nature of R group attached to nitrogen atom of sulfinylamine[161]. Thus when substituted fluorenylidene triphenylphosphoranes (122) reacted with N-sulfinyl-p-toluenesulfonamide (121a) on S=O bond of (121a) to give S-imide (123) and phosphine oxide analogous to Wittig reaction . On the other hand, the same ylid intermediates (122) attack on N=S bond of N-sulfinyl-p-nitroanilines (121b) to yield sulfines (124) and iminophosphoranes (125) (scheme I.43).

A.2.4. 12 Reaction of phosphorane intermediates with o-hydroxy benzaldehyde

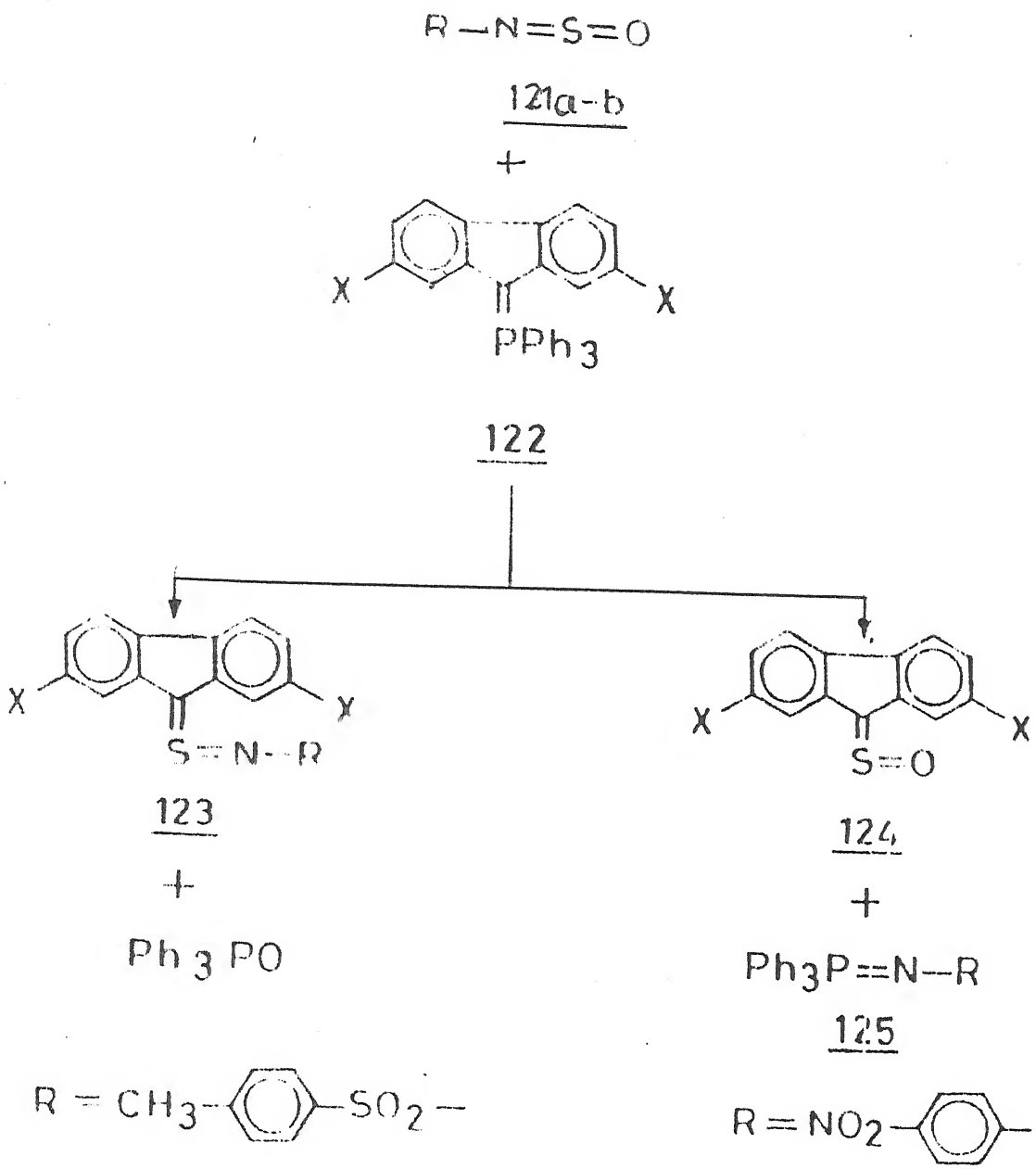
O-hydroxybenzaldehydes (126) reacted with carbonyl stabilized phosphorane intermediates (127) to give o-hydroxy chalcones (128)[162] (scheme I.44)

A.2.4.13 Reaction of phosphorane intermediates with isonitroso ketones

Alkylidene triphenylphosphoranes (129) in contrast to corresponding sulfuranes and arsoranes, on treating with ∝ --isonitrosoketones (130) gave PhC(: CH_2) CCH_3 : NOH (131)[163] (scheme I.45).

A.2.4.14 Reaction of phosphorane intermediates with acinitro -esters :

Scheme 1·43


R—N=S=O
121a-b
+
X
X
PPh3
122
X
X
S=N—R
123
+
Ph3PO
R = CH3— —SO2—
X
X
S=O
124
+
Ph3P=N—R
125
R = NO2— —

Reaction of ethoxy carbonyl methylene triphenylphosphorane with acinitroesters afforded α,β- unsaturated carboxylic esters[164] (scheme I.46).

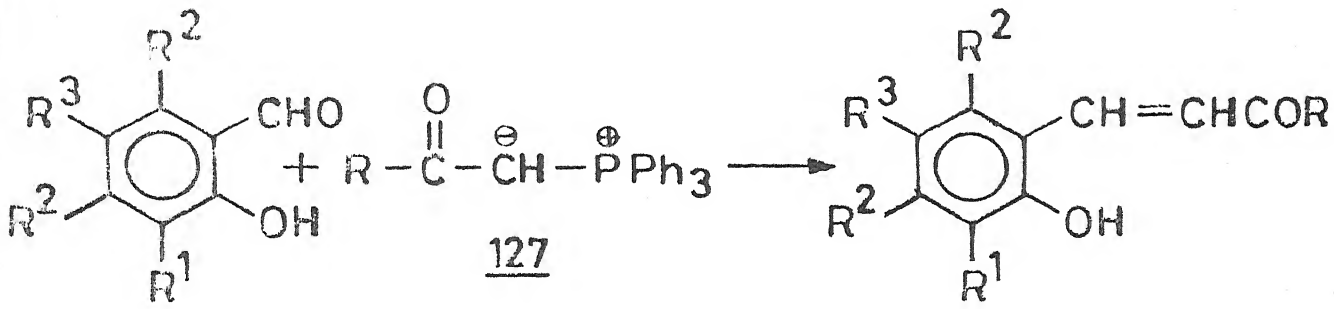
I.B ARSORANE INTERMEDIATES (ARSONIUM YLIDS)

With the investigations into the chemistry of phosphorane intermediates which assumed the status of a versatile carbonyl olefinating reagent in a wide variety of syntheses, curiosity aroused among the scientists to explore the chemistry of the heteroatom next to the phosphorus in V group of the periodic table . As expected from the electronic configuration and analogy to that of the phosphorus atom, trisubsitituted arsenic derivatives act as a Lewis base, having greater nucleophilicity as compared with the analogous trisubstituted phosphorus derivatives and undergo quaternization with substituted alkyl halides to form the quaternary arsonium salts.

The evolution of the chemistry of arsorane intermediates readily began with the earliest report of Michaelis[165] who attemped to prepare an arsorane intermediate (137) by the action of sodium hydroxide on phenacyltriphenylarsonium bromide (136), but he could not assign correct stucture to it. Since then this field remained dormant until Krohnke[166] suggested the correct structure to the ylid, phenacylidenetriphenylarsorane (138) (scheme I.47)

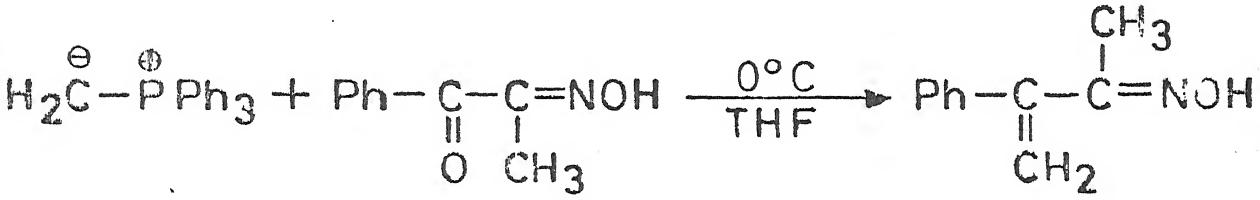
An ab initio LCAO-MO-SCF study [55] of the structure of model

SCHEME I·44



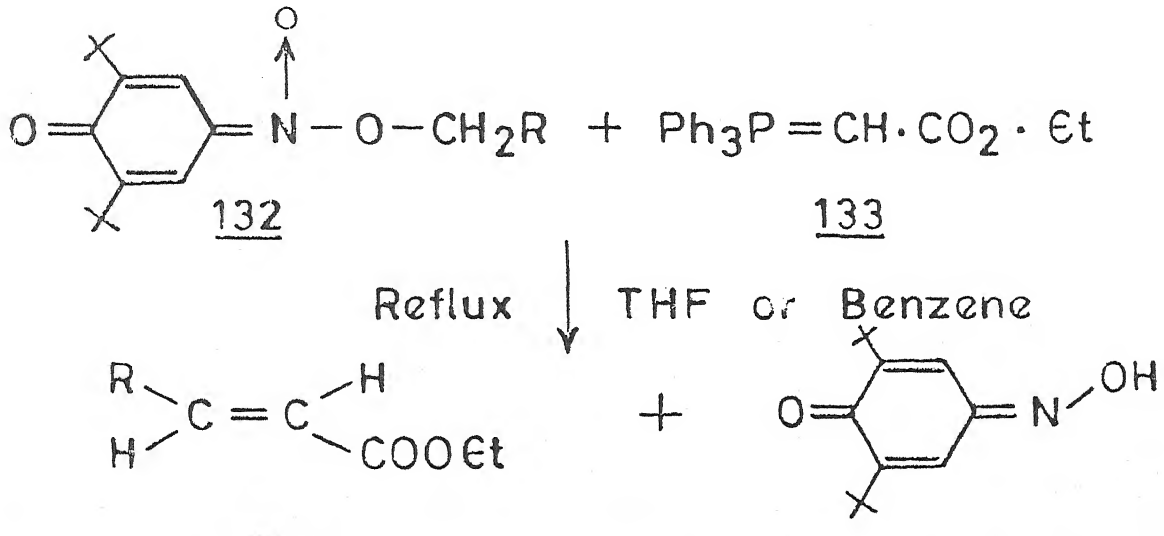
126 127 128

SCHEME I·45



129 130 131

SCHEME I·46



132 133 134

ylid methylenearsorane shows a planar stereochemistry at the ylidic carbon atom . The As-C bond length in methylene arsorane is 1.782 A. This results has been rationlized in terms of max. heteroatom C-π overlap.

In IR spectra of p-substituted phenacyclidene-triphenylarsenanes (139) the frequencies which characterize the conjugated bond system As=CH-C=O fluctuate between 1505 cm^{-1} and 1525 cm^{-1} . The pK_a values of the series of conjugate acids of the ylid were detected potentiometrically . It is found that the greater the electronegativity of the substituent at p-position, the greater will be the acidity of arsonium salts. The arsorane intermediates are found to be 200-300 times more basic than the analogous phosphonium compounds . Thus, As-atom plays a smaller part than P-atom in the distribution of negative charge.[167]

X-ray photoelectron spectral studies made very recently [168] of carbonyl stablized arsorane intermediates (139) have revealed that arsoranes have more tendency to exist as an ylid form. The arsoranes have been found to have greater tendency to exist as ylid structure than do the phosphoranes.[168]

Later on, Jhonson [169] and Nesmeyanov[170] isolated several stable arsorane intermediates and reported their reaction with carbonyl system to afford olefins in a manner analogous to that of phosphorane intermediates. In the recent years, arsorane intermediates have been utilized as a typical intermediate in the synthesis of a wide variety of acylic, cyclic and heterocyclic systems as releaved by increasing number of publications.[169-174]

I.B.1. GENERATION OF ARSORANE INTERMEDIATES (ARSONIUM YLIDS)

B.1.1. Arsorane intermediates from arosium salts (salt method)

The arsorane intermediate (143) are usually prepared by the action of suitable bases on the arsorium salts[175](142) obtainable from trialkyl or triarylarsine and alkyl halides (scheme I.48). The reaction is usually carried out in a non-polar solvent, though sometimes more polar solvents is advantageous. Some arsonium salts are prepared without using a solvent. [166]

The strength of base necessary for the removal of α —hydrogen from arsonium salts (142) depends upon the substituents R on the potential ylid carbanion (143). Recently, Nesmeyanov et al.[167] have reported that the generation of arsorane intermediate from arsonium salts requires stronger bases than are necessary for the generation of analogous phosphorane intermediates . Variety of bases used for generation of ylids are phenyllithium, [176-180] potassium tert-butoxide,[169] methanolic potassium hydroxide,[166] sodamide[181] and sodium hydride.[169] The variety of solvents used are benzene,[169] ether,[182,183] chloroform[182], methanol,[167,181], ethanol[182] and dimethyl sulfoxide.[172]

The non-stabilized, arsorane intermediates, which are incapable of being isolated are handled entirely in the solution and used up in subsequents reactions. Only those ylids in which carbanion is delocalized due to resonance,[166,175,177,181,182] have been isolated as pure,

crystalline substances by the action of suitable bases on their corresponding arsonium salts.

B.1.2 Arsorane intermediates by other methods

In addition to above cited salt method, several other methods have also been reported in the literature as described below :

B.1.2.1 By the interaction of triphenylarsine with carbene intermediates

Reactive carbene intermediates (144) when reacted with triphenylarsine yield arsorane intermediate directly (145)[172,184] (scheme I.49).

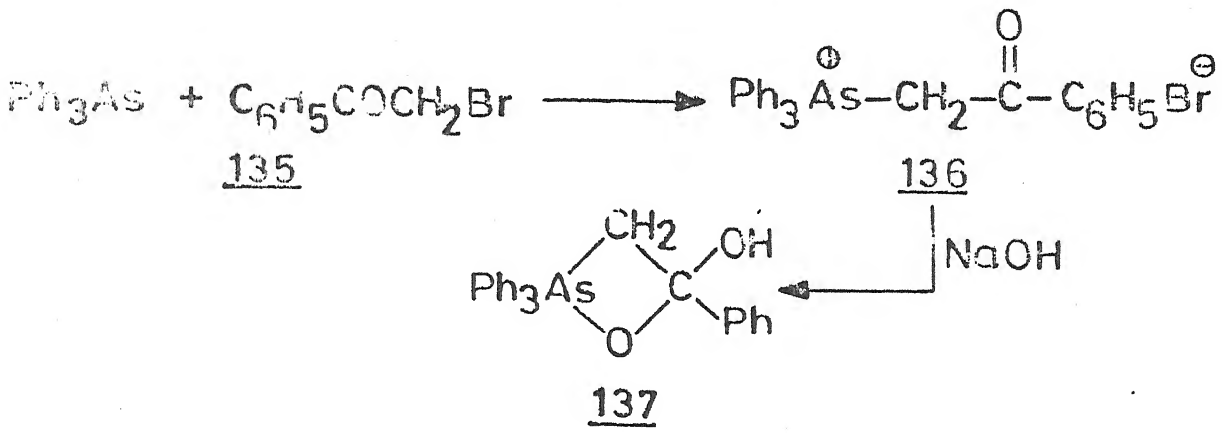
B.1.2.2 From the active methylene compounds

D.Lloyd and M.I.C. Singer[173] reported the successful formation of arsorane intermediates (146 & 149) by the reaction of active methylene compounds (147) with triphenylarsine oxide (148) in presence of either phosphorus pentaoxide with acetic anhydride or phosphorus pentaoxide with triethylamine (scheme I.50).

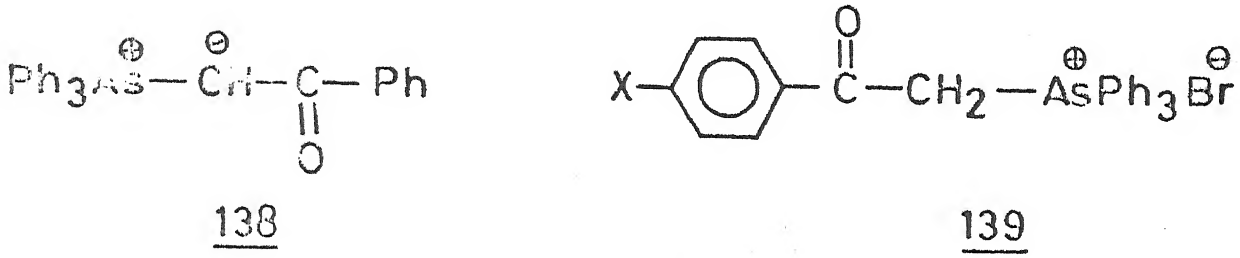
B.1.2.3. From triphenylarsine dichloride

The synthesis of arsorane intermediates (152) is also made possible by Z.Horner and H.Dediger [185] if allowing the interaction of triphenylarsine dichloride (150) with the compounds having active methylene group (151) (scheme I.51).

SCHEME I.47

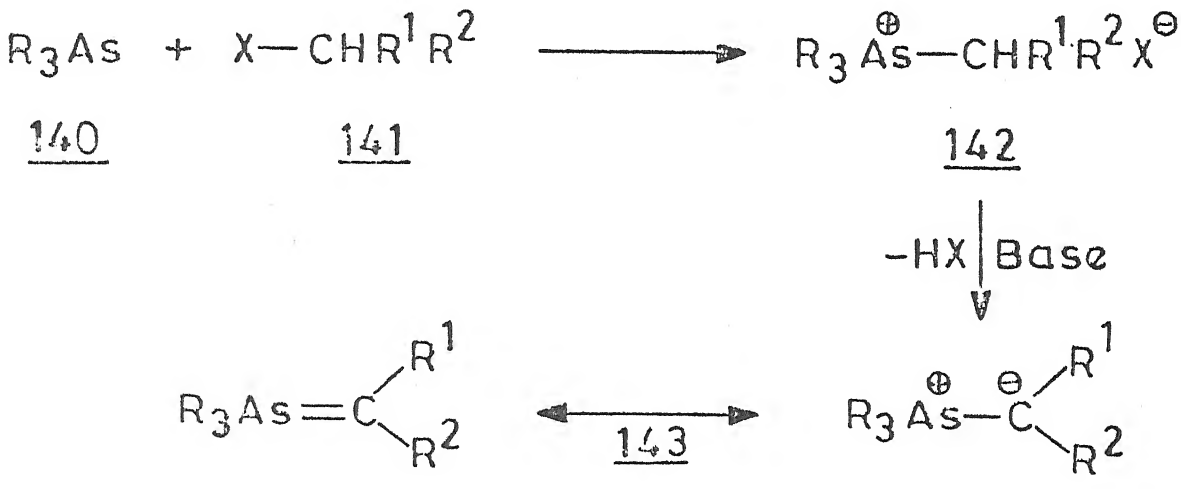


135 136 137



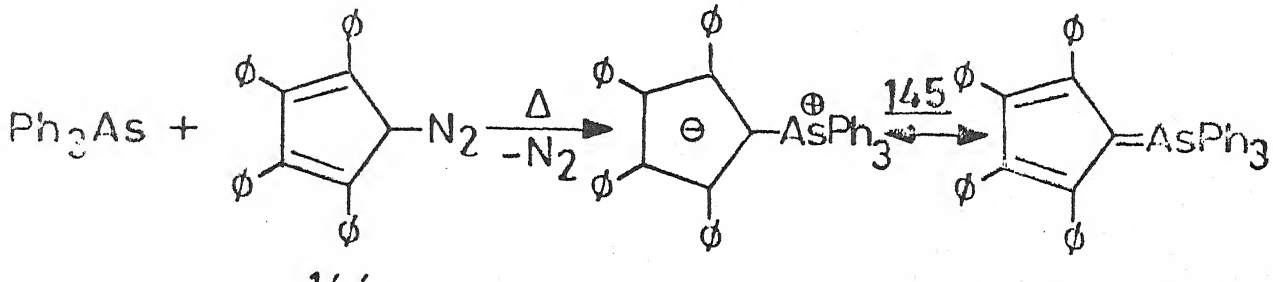
138 139

SCHEME I.48



140 141 142 143

SCHEME I.49



144 145

D.Lloyd et al. (1971) [186] also prepared arsorane intermediates by the reaction of dibromocyclopentene and triphenylarsine followed by the treatment with bases.

B.1.2.4. By transylidation reaction

Carbonyl stabilized arsorane intermediates (155) were obtained from unstable (153) ones via transyldidation reaction which involve the action of two moles of reactive but unstable ylids (153) on acyl halide [169,187-189] (scheme I.52).

B.1.2.5 By the cathodic reduction of arsonium salts

Misra et al. (1982)[190] prepared arsorane intermediates by the cathodic reduction of arsonium salts in methanol in presence of carbonyl compounds.

B.1.2.6 From $Me_3As=CHSiMe_3$

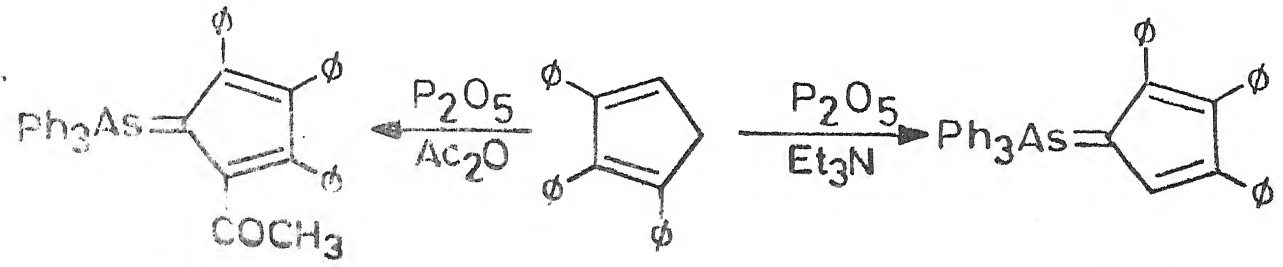
Tetramethylmethoxyarsorane (158) was prepared by the reaction of $Me_3As=CHSiMe_3$ (156) with methanol .[191] (scheme I.53)

I.B.2. REACTION OF ARSORANE INTERMEDIATES

B.2.1 Hydrolysis of arsorane intermediates

The stable arsorane intermediates remain unchanged in presence of water whereas non- stabilized arsorane intermediates (159) are hydrolysed to give arsonium hydroxide (160) by simple proton transfer (scheme I.54) . This is in contrast to the phosphorane intermediates which are rapidly decomposed to hydrocarbons . But stabilized arsonium intermediates(161) on

SCHEME I. 50



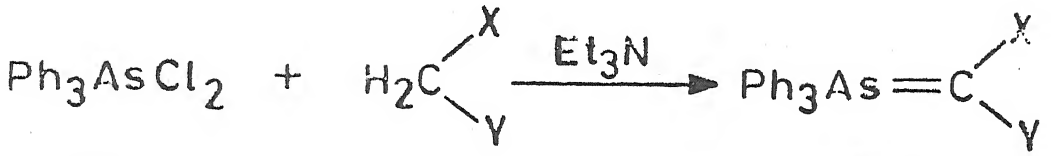
146 147 149

+

$Ph_3As{=}O$

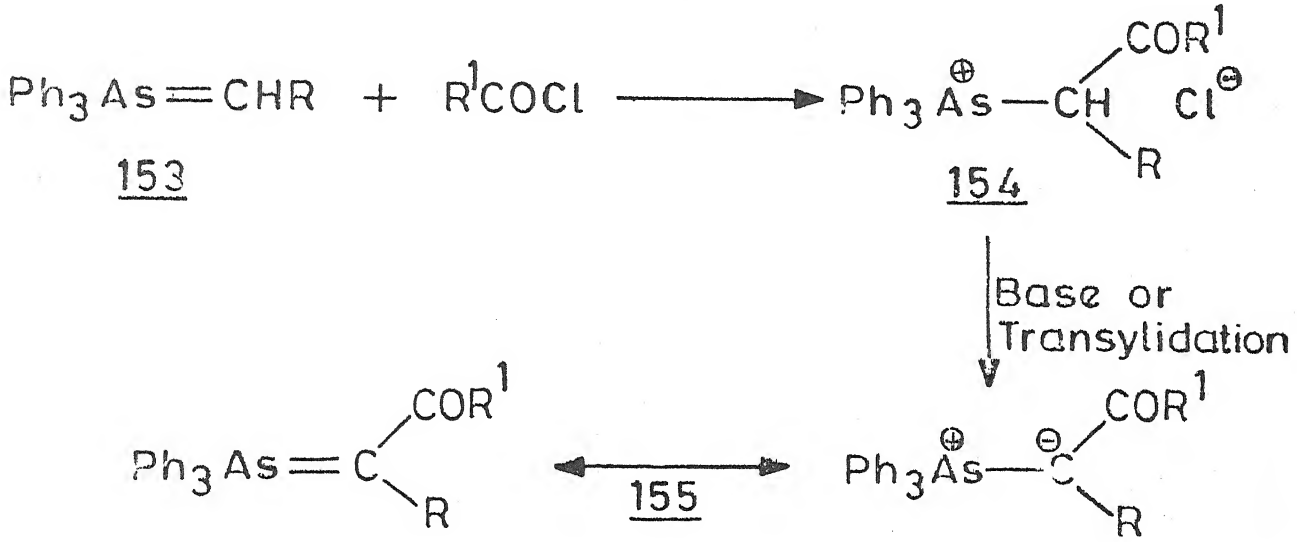
148

SCHEME I. 51



150 151 152

SCHEME I. 52



153 154 155

slight warning in presence of a base and alcohol are hydrolysed to hydrocarbons (162) and triphenylarsine oxide [169,175,185] (scheme I.55)

B.2.2 Alcoholysis of arsorane intermediates

Alcoholysis of p-nitrobenzylidene triphenylarsenane (164) generated from its arsonium salt (163) with ethanolic sodium hydroxide gave 4,4'-dinitrostilbene (165) ,triphenylarsine (166), 4,4'-dinitrobenzyl (167), p-nitrotoluene (169) and triphenylarsine oxide (168) [192] (scheme I.56) .

B.2.3 Thermolysis of arsorane intermediates

Jhonson and Schubert [169] were frist to carry out the thermolysis of stabilized ylids, phenancylidene triphenylarsenane (170) by heating it in toluene and obtained trans-1,2,3-tribenzoylcyclopropane (171) along with triphenylarsine (scheme I.57). The mechanism of reaction was thought to operate via carbenoid intermediate . Similarly Nesmeyanov et al. [192] have also supported the formation of cyclopropane through the thermolysis of ylid. Thermolysis of a semistabilized arsorane intermediate in benzene ether solution, on the other hand, gave triphenylarsine and a mixture of cis- and trans-stilbenes in ratio[193] 1:5.2.

B.2.4. Alkylation of arsenanes

Reaction of alkyl halides with carbonyl stabilized arsorane intermediates (172) gave O-alkylated salts [169] (173) in a manner

SCHEME I.53

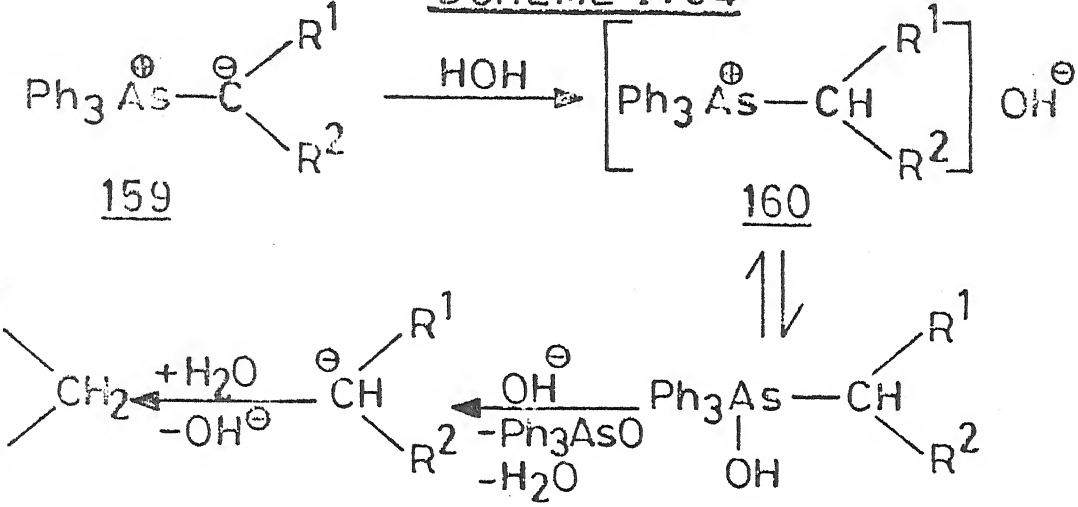
$Me_3As{=}CH\ SiMe_3 + CH_3OH \longrightarrow Me_3SiOMe + Me_3As{=}CH_2$

156 157

$Me_3As{=}CH_2 + CH_3OH \longrightarrow Me_4AsOMe$

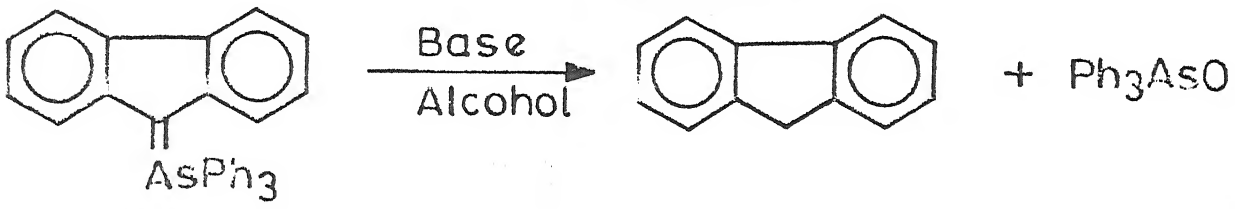
157 158

SCHEME I.54



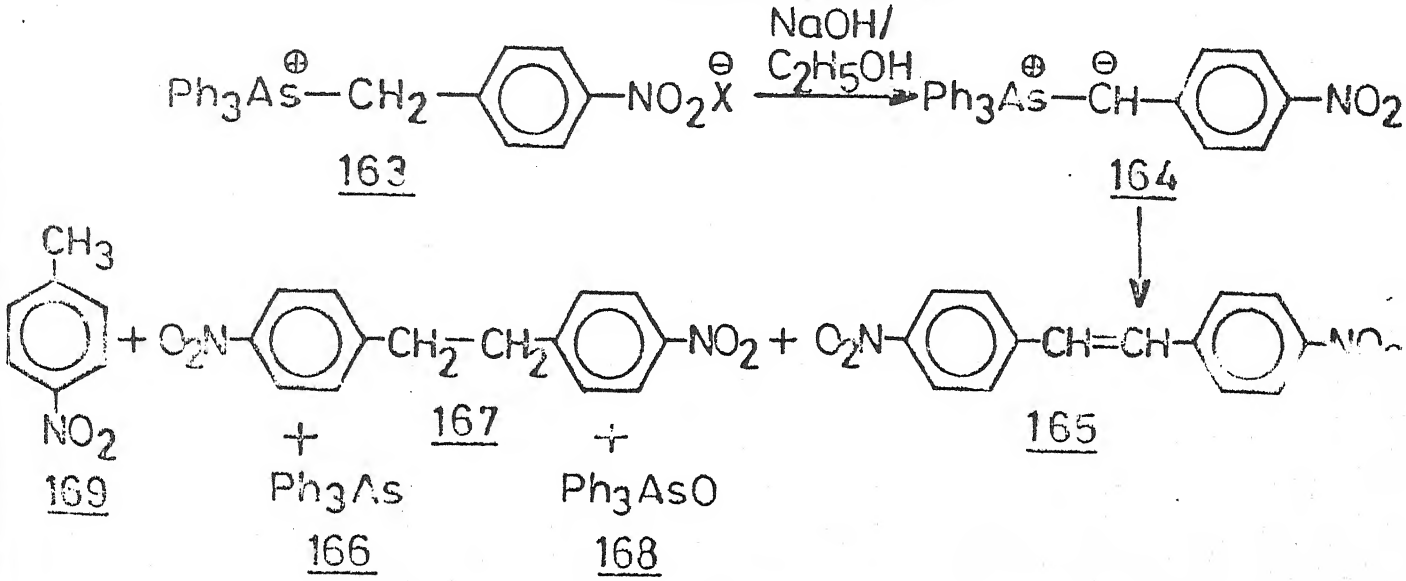
159 160

SCHEME I.55



161 162

SCHEME I.56



163 164 165 166 167 168 169

analogous to that of phosphorane intermediates [124] (scheme I.58), whereas the reaction of same ylid (172) with phenacyl bromide (174) underwent C-alkylation to give cyclopropane derivatives (175) [169] (scheme I.59).

B.2.5. Acylation of arsenanes

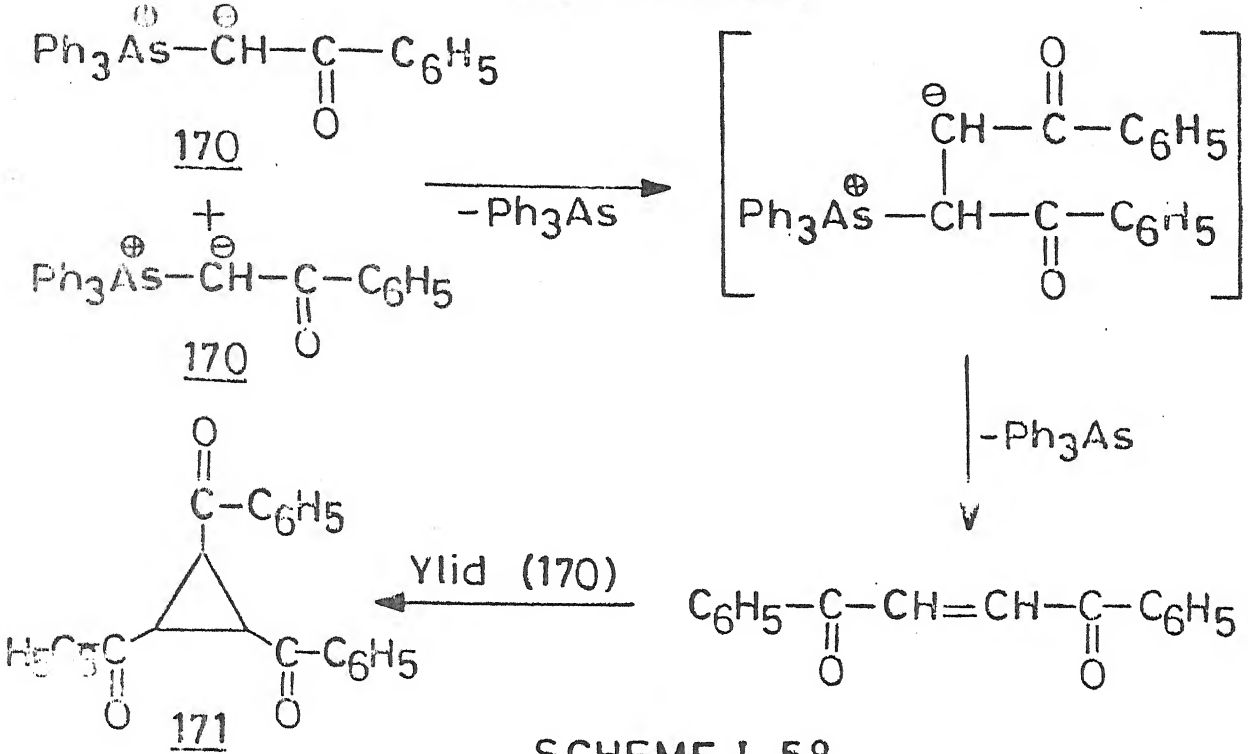
Acylation of non-stabilized arsorane intermediates (176) gave C-acylated arsonium salts (177) which on further treatment with base or starting ylid (176) via transylidation reaction yielded new carbonyl stabilized arsorane intermediates (178) [167,169] (scheme I.60). On the other hand, carbonyl stabilized arsorane intermediates (179) which exhibited two reasonating structures (179a-b) gave O-acylated and C-acylated products depending on the nature of acylating agents. [169] Thus, benzoic anhydride and acetic anhydride followed C-acylation to give new ylids (180) whereas benzoyl halides affected O-acylation yielding enolbenzonate (181) which was isomerized to the ylid (180) in presence of sodium acetate [169] (scheme I.61). Semi stabilized arsorane intermediates on acylation gave carbonyl stabilized ylids and arsonium salts. [187,188]

B.2.6 Reactions of arsenanes with multiple bonds

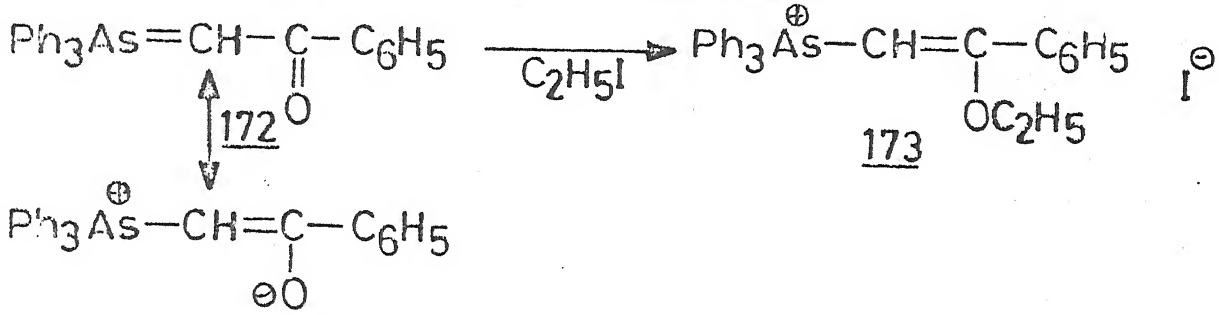
2.6.1. Carbonyl compounds (reaction with C=O)

The reaction of arsorane intermediates with carbonyl [178,183] compounds to give either olefins [169,172,175,182,184,195,196] or epoxide [178,182,197] or both

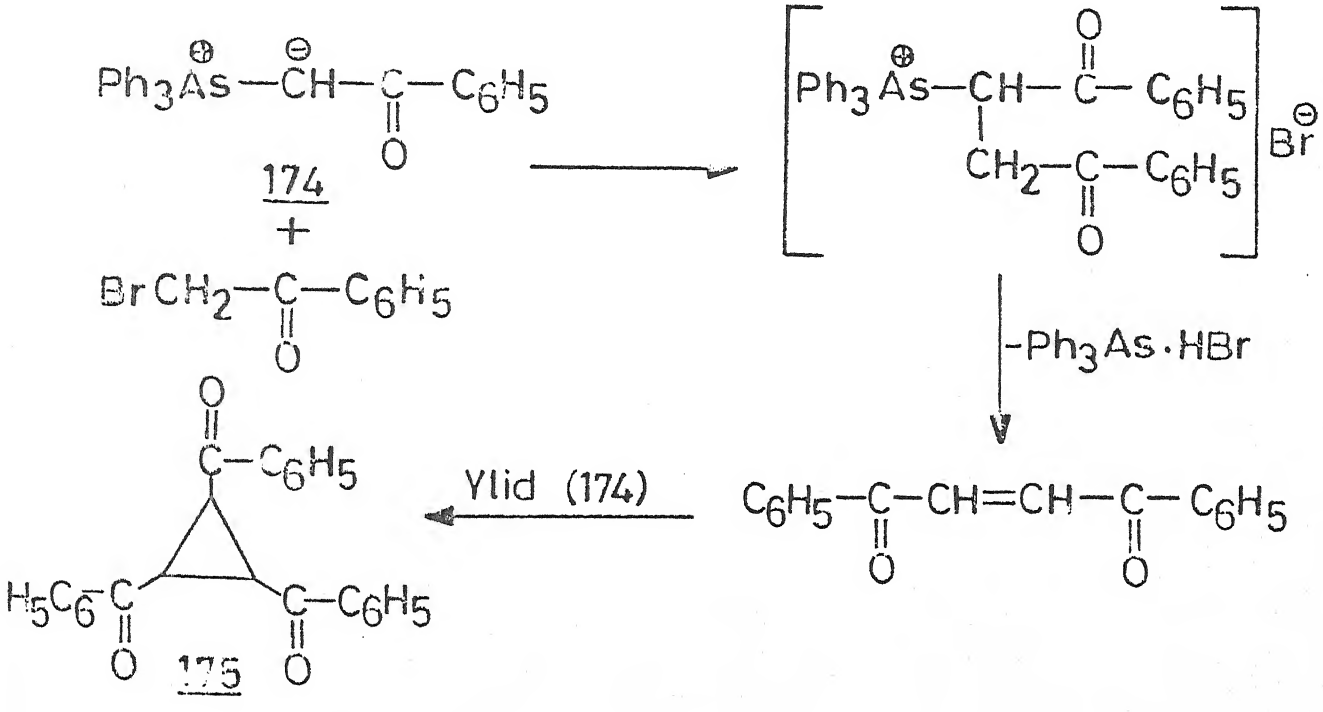
SCHEME I.57



SCHEME I.58



SCHEME I.59

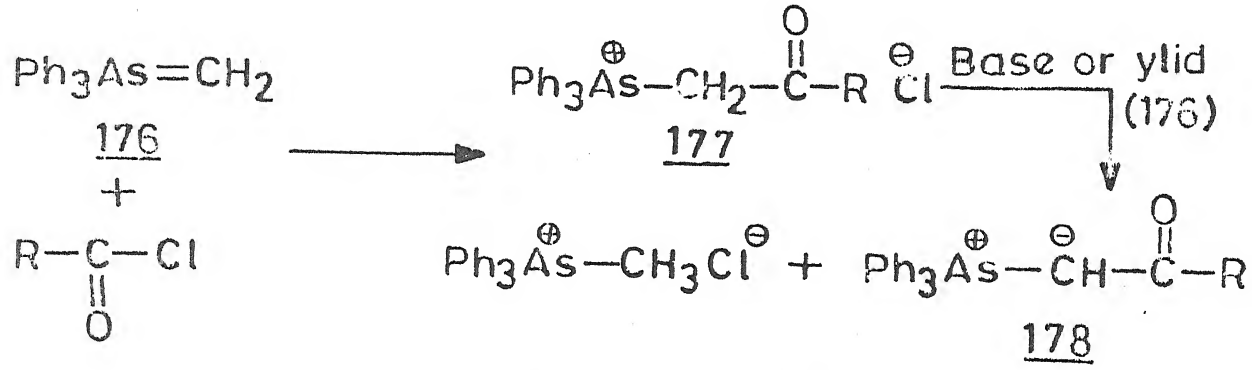


[178,183] in the same reaction,have attracted a good deal of attention of organic chemists. Thus, non-stabilized arsorane intermediate,[178] methelyne triphenylarsenane (182) reacts with benzophenone (183) to produce a mixture of triphenylarsine, diphenylacetaldehyde (185), the rearranged product of 1,1-diphenylethylene oxide (184), triphenylarsine oxide and diphenylethylene (186) (scheme I.62), whereas stabilized arsorane intermediates,[192,204] phenacyclidene triphenylarsenanes (187) with benzaldehydes (188) gave α,β-unsaturated ketones (189) only (scheme I.63)

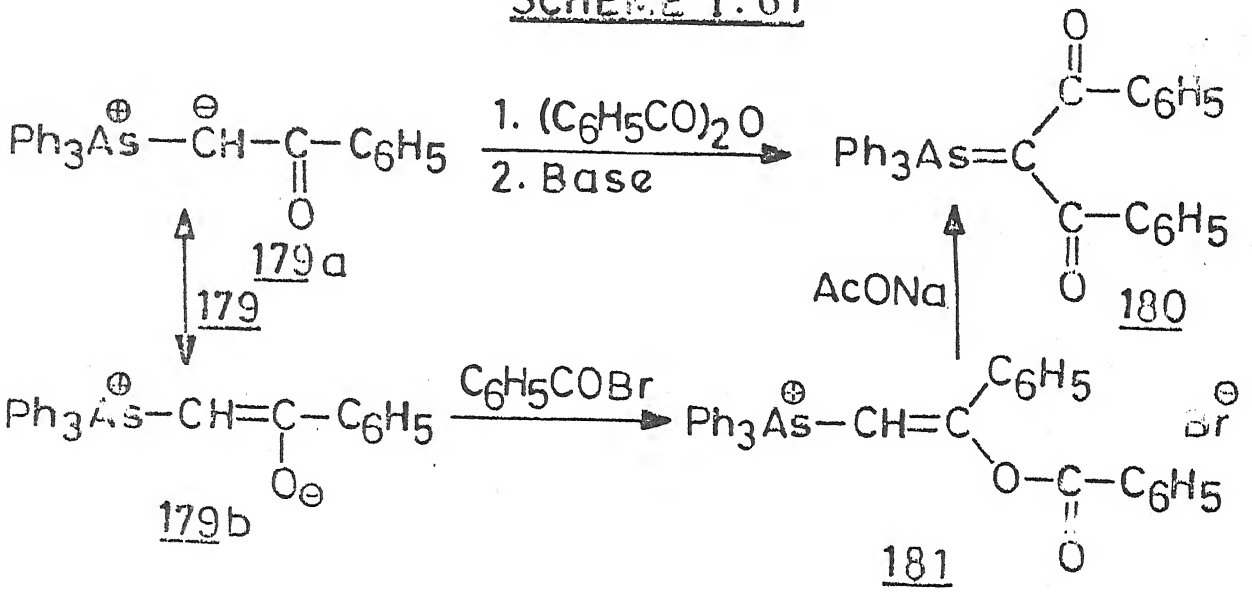
The behaviour of stabilized arsorane intermediates [169,170,175,205,206] paralleled to that of analogous phosphorane inermediates. It has also been reported that the arsorane intermediates are more nucleophilic than analogous phosphrane inermediates.[196] Recently, some stabilized arsorane intermediates (187) have been observed to undergo reaction with ketones (190) which fail to react with phosphonium analogous (scheme I.63)

The behaviour of non-stbilized arsorane intermediates[178,177] is analogous to sulfonium ylids, [198] whereas the stable arsenanes behave like phosphoranes towards carbonyl compounds. However semi-stabilized arsorane intermediates hold a position intermediate between stabilized and non-stabilized ylids yielding either olefin or epoxide or both in the same reaction as reported by Jhonson[199] and Nesmeyanov.[200] Thus,benzylidene triphenylarsenane (191)[197] and p-nitrobenzylidenetriphenylarsenane (192)[200] gave approximately equimolar amounts of both olefin

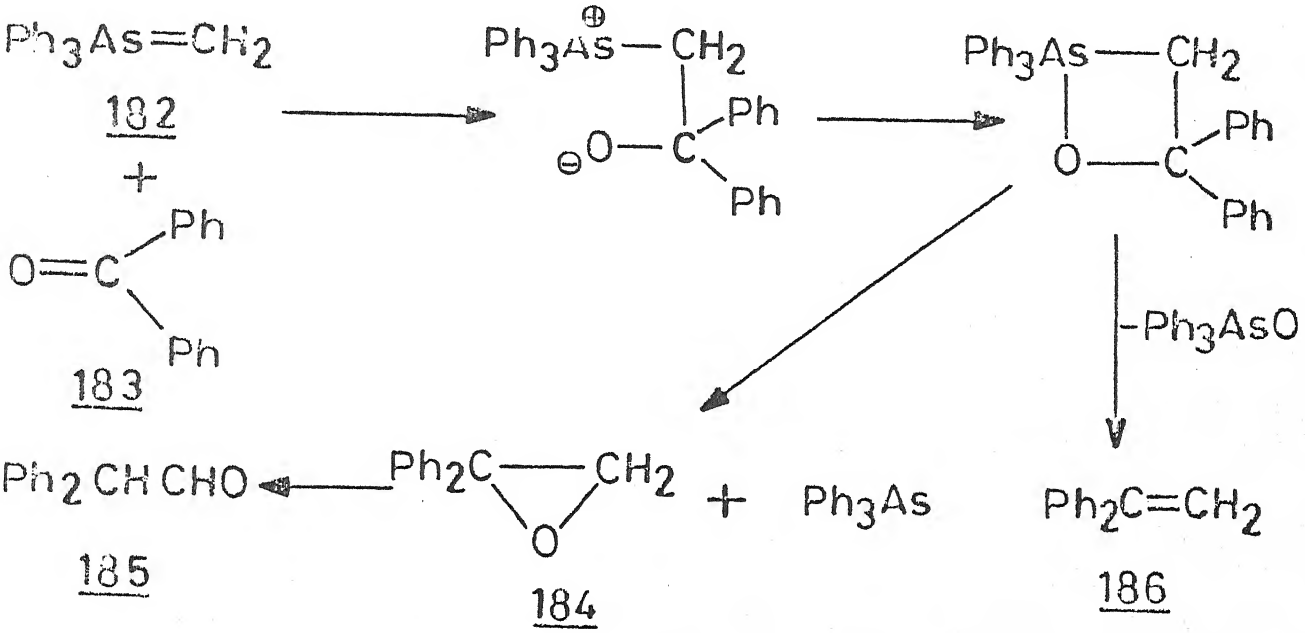
SCHEME I.60



SCHEME I.61



SCHEME I.62

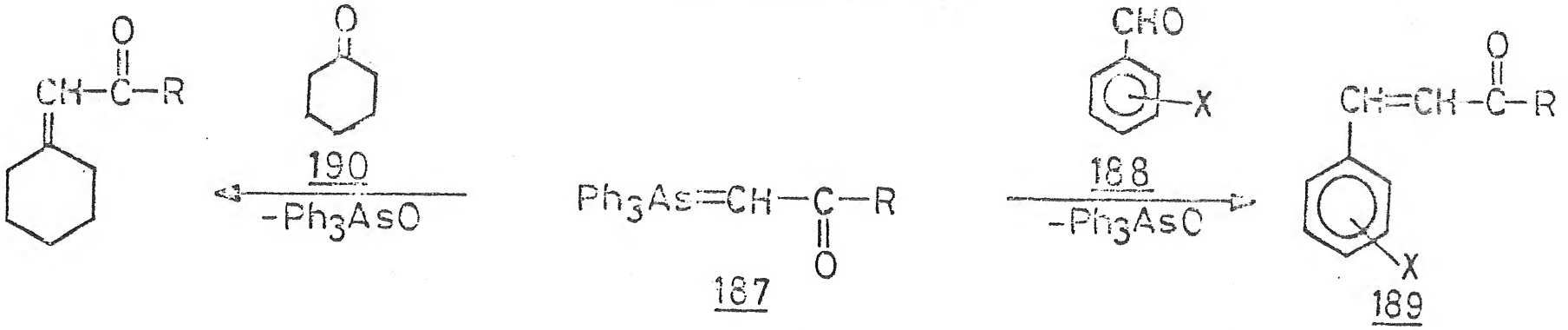


(193) and epoxide (194) (scheme I.64). Later on, the exact path of reaction of semi-stabilized arsorane intermediates was studied by Trippett et al.[192]. Who reported that the semi-stabilized p-substituted benzylidene-triphenylarsorane intermediates (195) would give either olefin (196) or epoxide (197) but not both in the same reaction depanding upon the nature of substituents present at ylid carbanion (scheme I.65)

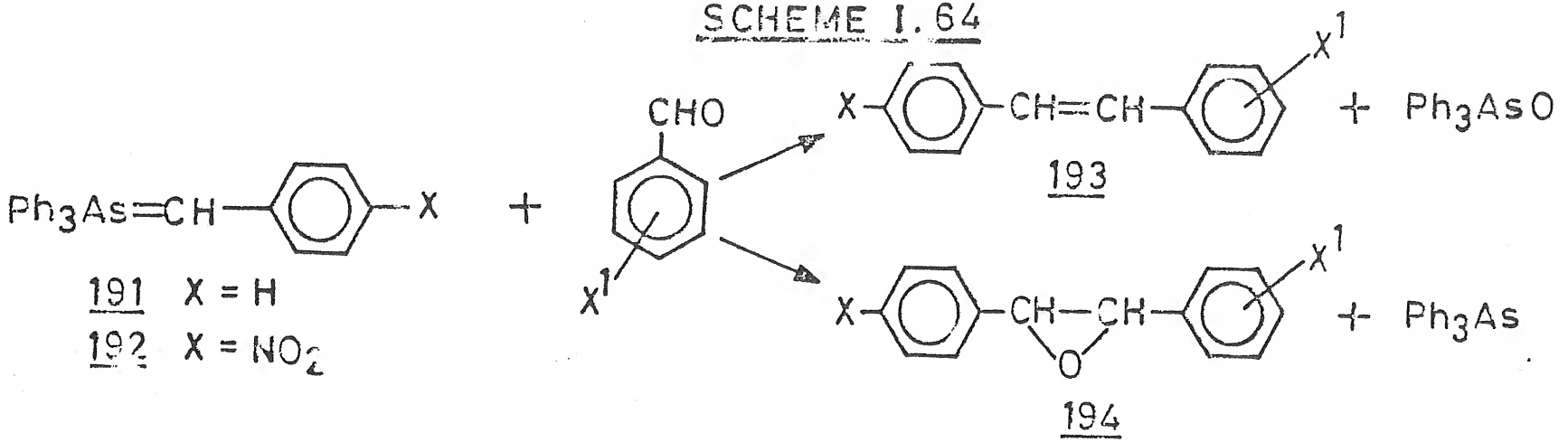
With a view to ascertain the exact course of reaction, recently Tewari et al.[201,202,207,208] have investigated several semi- stabilized arsorane intermediates having electron-attracting and releasing groups observed that olefins were the exclusive products of the reactions when groups were of electron attracting nature.

In addition to the effect of substituents on ylidic portion, the effect of solvents and bases also plays an important role in determining the course of reaction. Thus, p-chlorobenzylidene-triphenylarsenane (199) and benzylidenetriphenylarsenane (199) generated from its salts (198) with sodamide in benzene gave olefins (200) whereas epoxide (201) were formed exclusively when ylid (199) was generated with sodium ethoxide in ethanol [203] (scheme I.66). I.Gosney, T.J. Lillie and D.Lloyd (1977)[209] carried out a series of reactions to study the effect of sub-stituents on arsenic atom during the course of reaction of ar-sorane intermediate with carbonyl compounds and reported that the electron donating groups at arsenic atom favour alkene formation while electron attracting substituents linked to arsenic atom

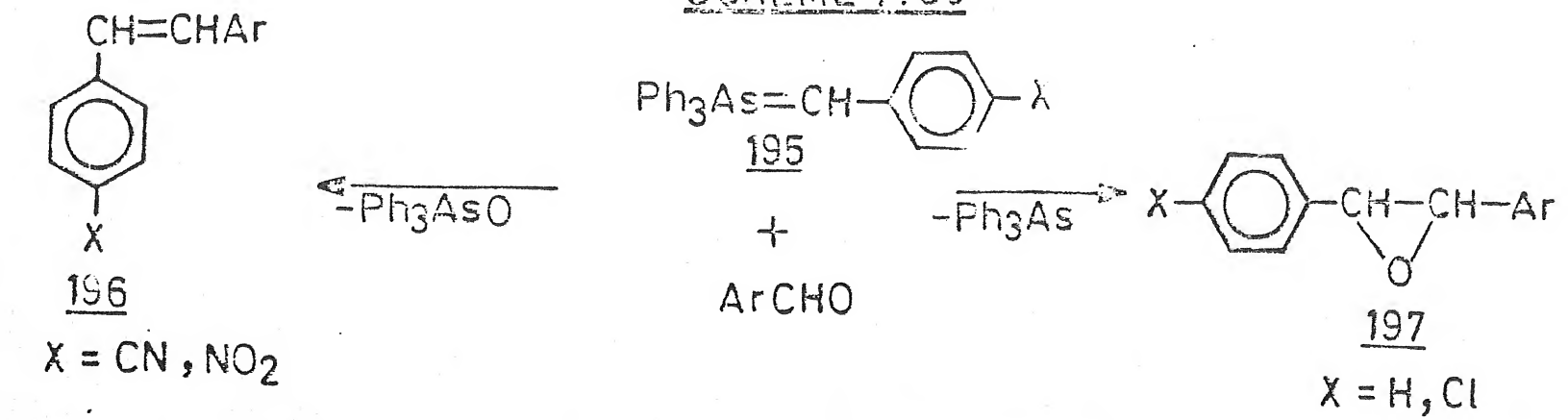
SCHEME I.63



SCHEME I.64



SCHEME I.65



mould the reaction mechanism to affored epoxide.

Non-stabilized arsorane intermediates (202) with O-aminocarbonyl compounds (203) gave various substituted indoles (204)[171] (scheme I.67).

2.6.2. Reaction with N=O bonds (Nitroso compounds)

The arsorane intermediates (205) resemble very closely to the sulfurane intermediates in their reaction with nitroso compound (206) giving oxime (207)[199,210] (scheme I.68). In no case were anils obtained as in the case of corresponding phosphorane intermediates [211].

2.6.3. Reaction with C=N bonds (Schiff's bases)

In the reaction with Schiff's bases (209), arsorane intermediate (208) resembles sulfurane intermediates rather than phosphorane intermediate yielding aziridine derivatives (210)[182,212] (scheme I.69).

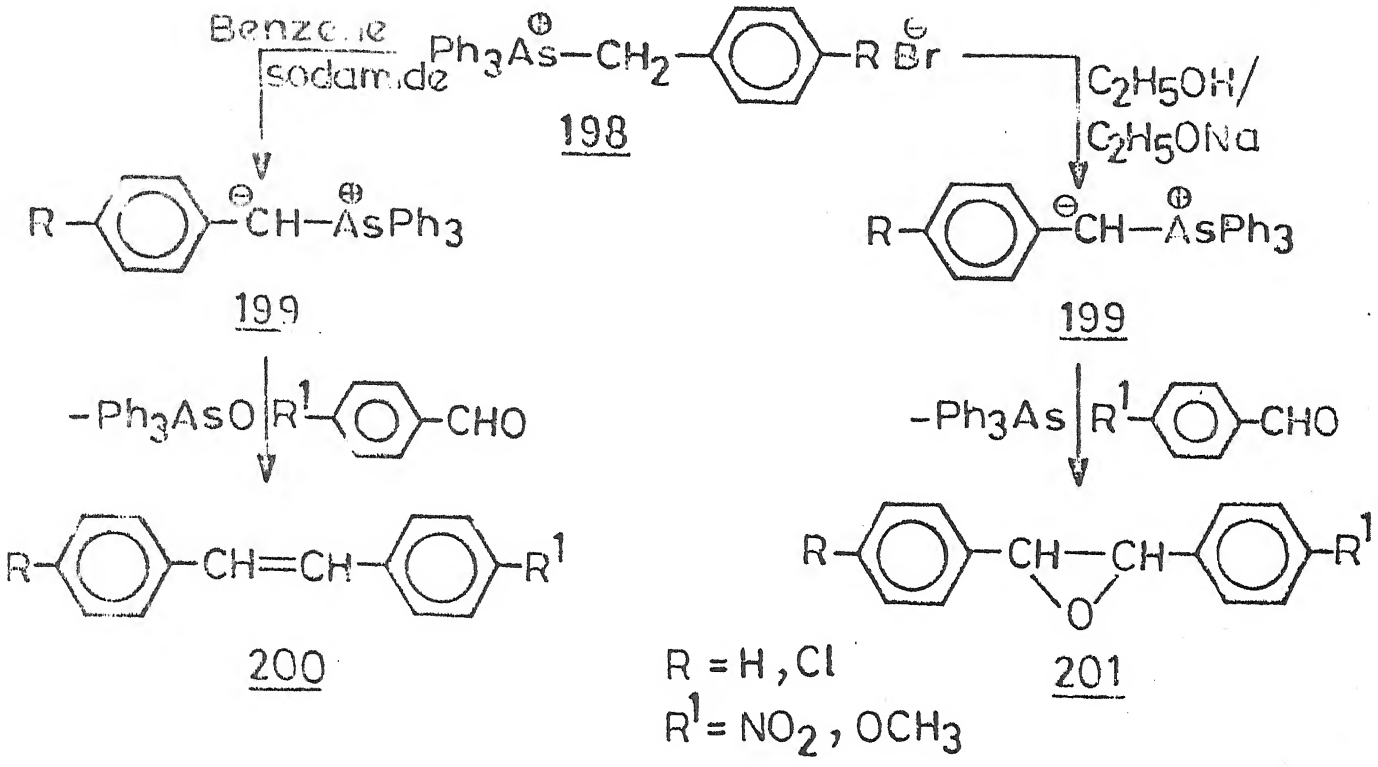
2.6.4. Reaction with C=C bonds

The activated double bonds containing mono- or dicarbonyl systems are attacked by arsorane intermediates to give cyclopropane derivatives (211) [182,192] (scheme I.70).

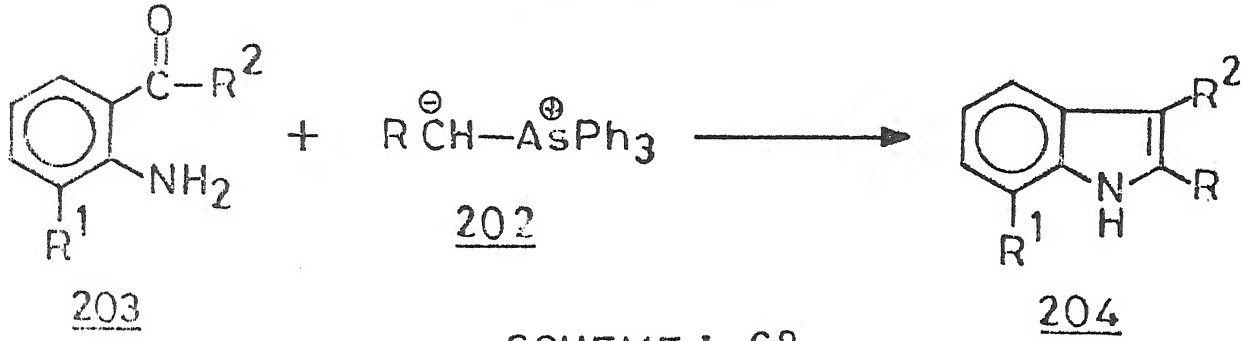
2.6.5. Reaction with C≡C bonds

Trippett and Walker[182] found that p-bromophenacylidene-

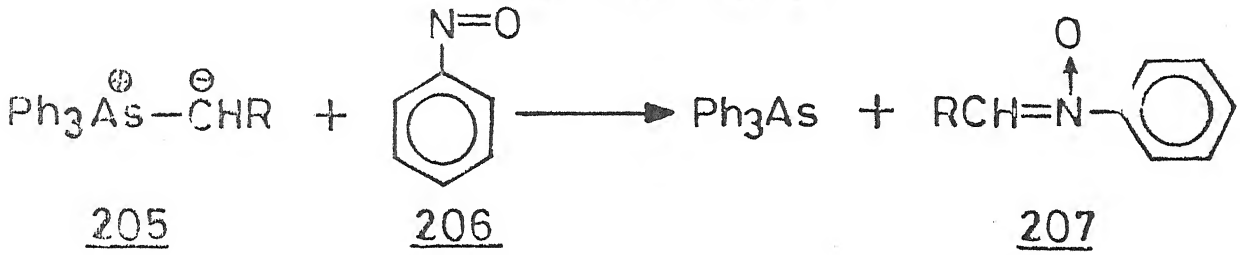
SCHEME I.66



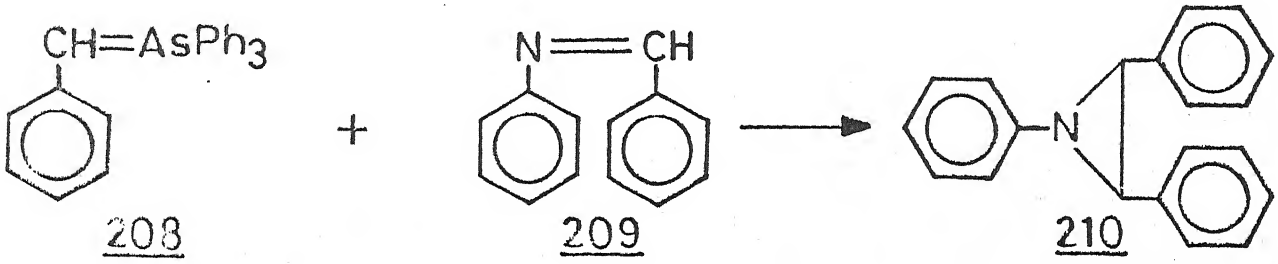
SCHEME I.67



SCHEME I.68



SCHEME I.69



triphenylarsenane (212) reacted readily with dimethyl acetylene dicarboxylate (213) to give a new arsorane intermediate (215) through the intermediacy of a cyclic compound (214) (scheme I.71).

2.6.6. Reaction with C=S bonds

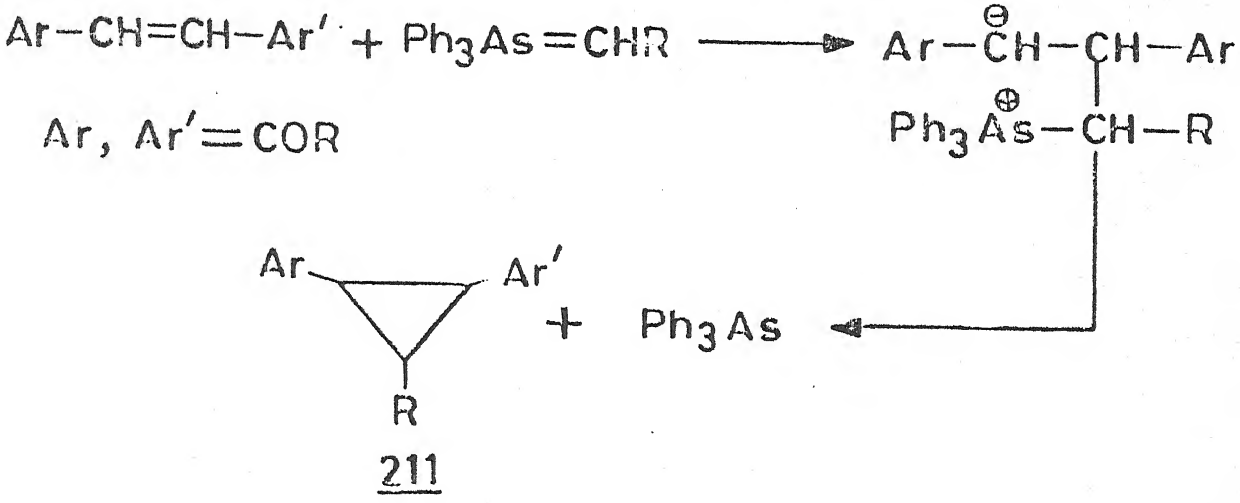
The arsorane intermediate (216) reacts with phenylsulfine (217) to give a stable sulfur containing arsorane intermediate (218)[182] (scheme I.72), whereas, the reaction of ethoxycarbonylmethylenetriphenylarsenane (219) with phenylsulphene (220) gives ethylcinnamate (223), triphenylarsine and new arsorane intermediate (221). It is assumed that ethyl cinnamate (223) is formed via transepisulphone (222) [165] as shown in scheme I.73.

Recently , Tewari et al.[136] have studied the reaction of some thioketones (225) with semi- stabilized arsorane intermediates (224) and observed that same normal Wittig product (226) was formed [136] (Scheme I.74). Later on, the author carried out the thiocarbonyl olefination of thiocoumarin (228) with semi-stabilized ylids (227)[216] (Scheme I.75).

B.2.7. Reaction of arsorane intermediate with aziridines

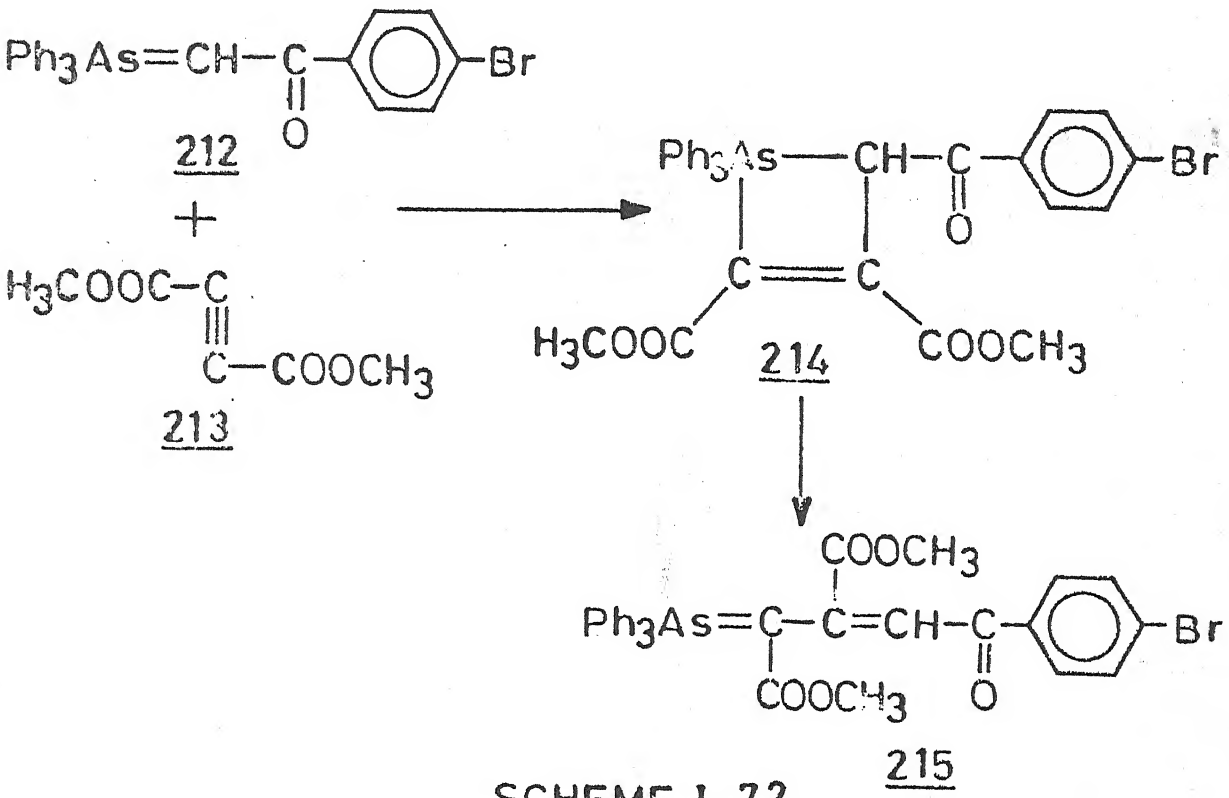
Jhonson [213] observed that the reaction of phenacyclidene-triphenylarsenane (230) with p-nitrobenzoylaziridine (237) in refluxing toluene afforded N-(γ -benzoyl- γ -triphenylarsonium-propyl) -4-nitrobenzamide (232). The reaction invovles the

SCHEME I. 70

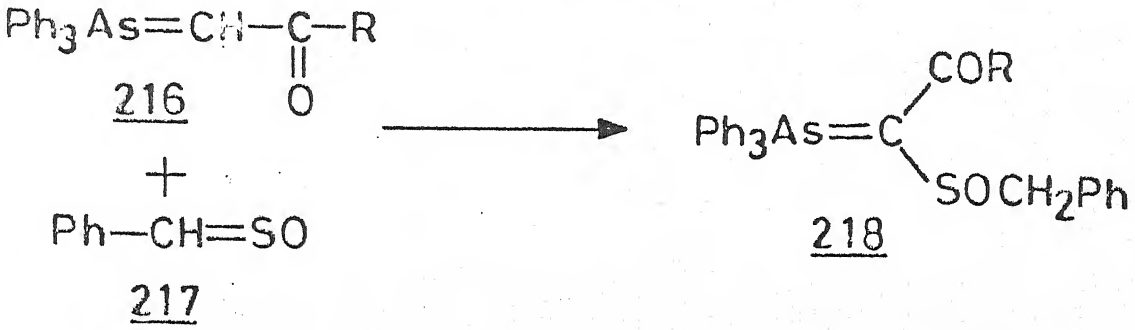


211

SCHEME I. 71



SCHEME I. 72



decomposition of intermediate formed by the nucleophilic attack of ylid carbanion on C-3 of aziridine (scheme I.76).

B.2.8. Reaction of arsorane intermediates with ∝-nitrosoketone

The reaction of non-stabilized ylid (233) with ∝-nitrosoketone (234) in tetrahydrofuran at 0° C gave 5-hydroxy- Δ^2 -isoxazoline (235) which on dehydration yielded isoxazole (236)[214] (Scheme I.77).

B.2.9. Reaction of arsorane intermediates with anilines

Recently, Bansal and sharma [174] have reported that the substituted phenacylidenetriphenylarsenanes (238) reacted with anilines (237) in presence of N,N-dimethylaniline to give 2-substituted indoles (239) (Scheme I.78).

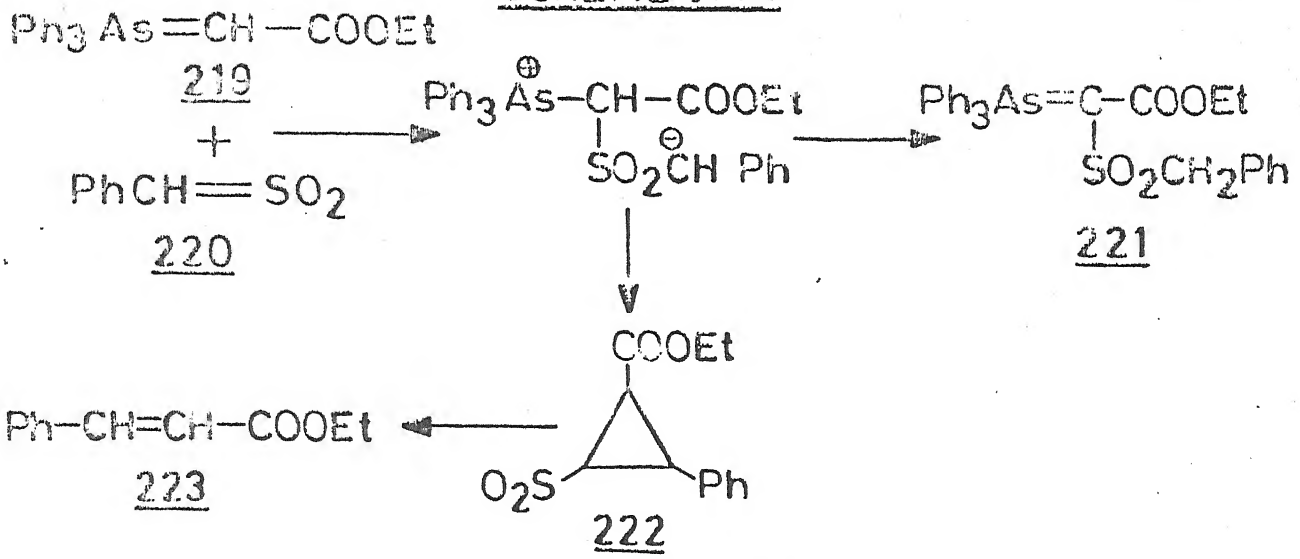
B.2.10. Reaction of arsorane intermediates with epoxide

The non-stabilized arsorane intermediates (240) undergo cyclization with ethylene oxide (241) to give oxarsolanes (242)[215] (Scheme I.79).

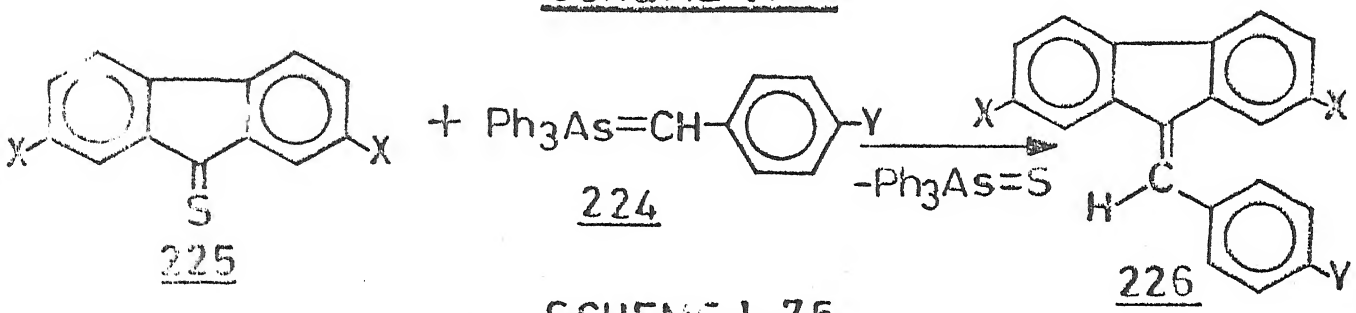
B.2.11. Reaction of arsorane intermediates with phenylhydrazines

Phenacyltriphenylarsonium bromide (244) reacted with phenyl hydrazine (246) in N,N-dimethylaniline under reflux to give substituted 3-phenyl-1,2-dihydrocinnolines (245)[217] (Scheme I.80).

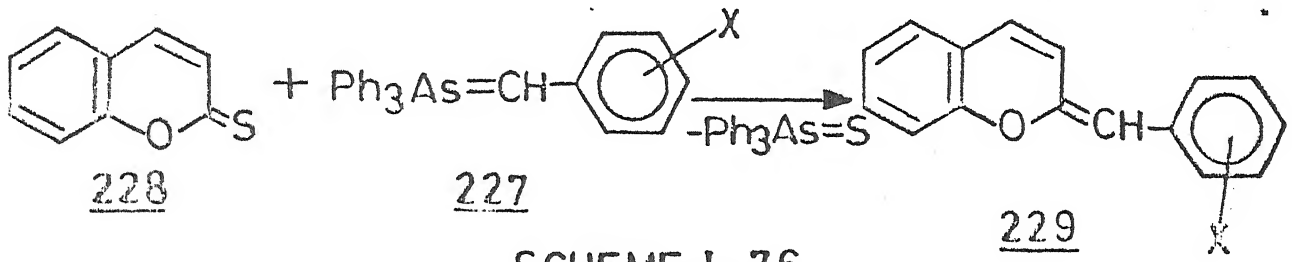
SCHEME I.73



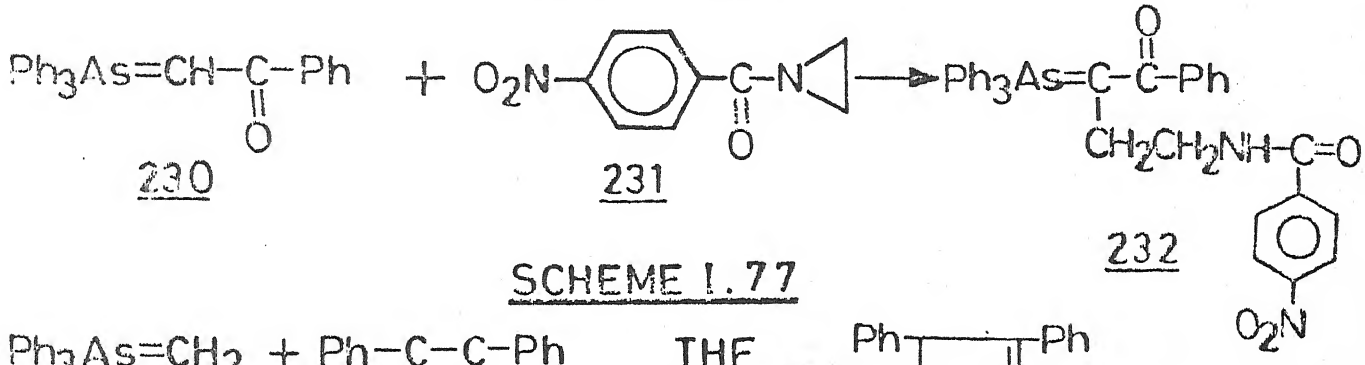
SCHEME I.74



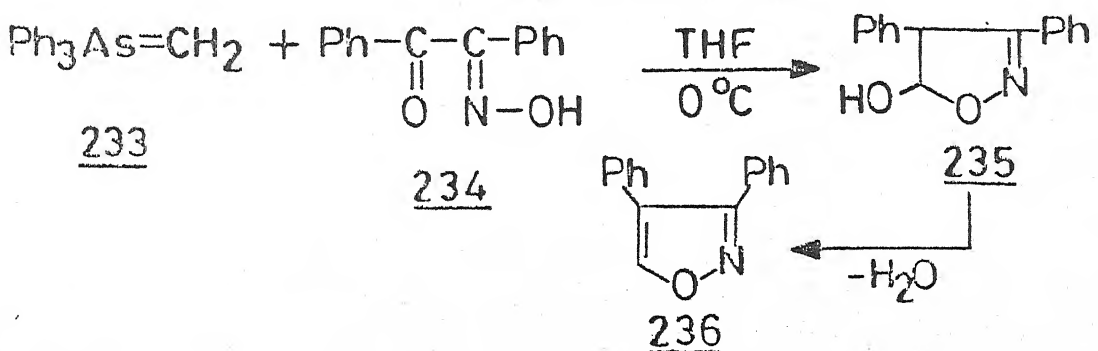
SCHEME I.75



SCHEME I.76



SCHEME I.77



B.2.12. Reaction of arsorane intermediates with ketones

In contrast to the cyanomethylenetriphenylphosphorane, the corresonding arsoranes (246) react with ketones to give α,β-unsaturated nitrile (247) in 23-87% yields.[218] This shows high reactivity of arsorane intermediates over corresponding phosphorane intermediates (Scheme I.81)

B.2.13. Reaction of arsorane intermediates with O-hydroxy benzaldehyde

Aldehydes (248) reacted with carbonyl stabilized arsorane intermediate (249) to give O-hydroxy chalcones (250)[162] (Scheme I.82)

B.2.14. Reaction of arsorane intermediates with α-chlorooximes

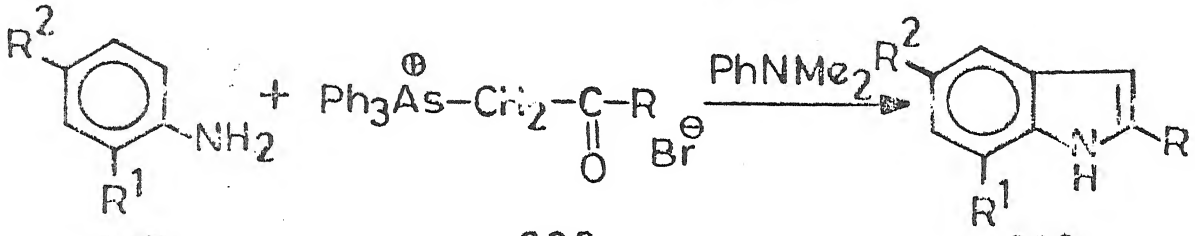
The reaction of α-chlorooximes (251) or the isomeric nitroso-chlorides (252) with keto stabilized triphenylarsonium intermediates (253) like corresponding sulfurane intermediates gave trans-5-acyl-Δ^2-isoxazolines [219] (254) (Scheme I.83).

B.2.15. Reaction of arsorane intermediate with α,β-unsaturated esters

Reaction of arsorane intermediates (255) with α,β- -unsaturated esters (256) gave cyclopropanes (257) in 40-43% yields [220] (Scheme I.84).

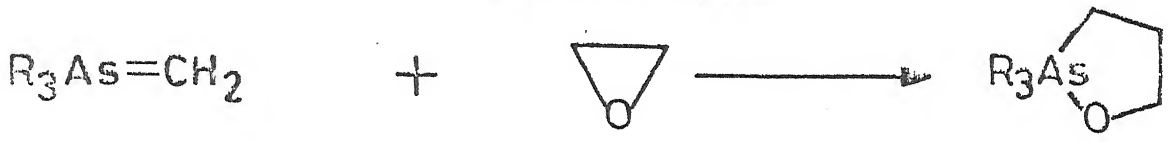
B.2.16. Reaction of arsenanes with aromatic diazonium salts

SCHEME I.78



237 238 239

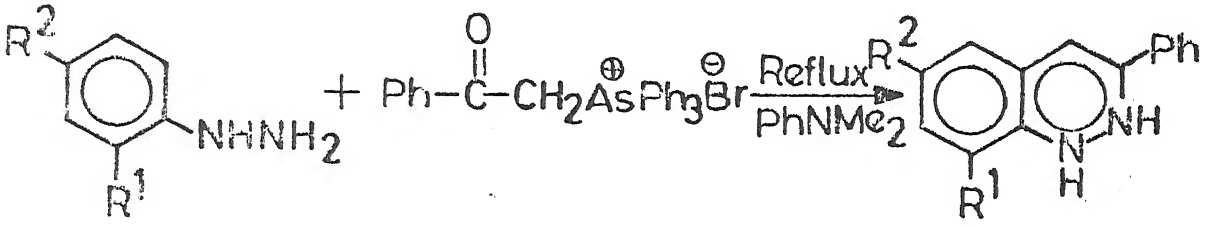
SCHEME I.79



240 241 242

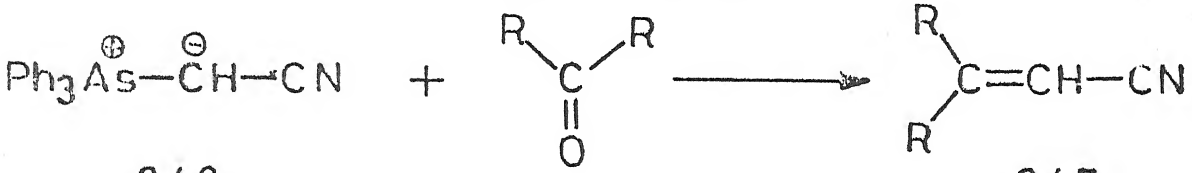
R = CH_3 , C_2H_5

SCHEME I.80



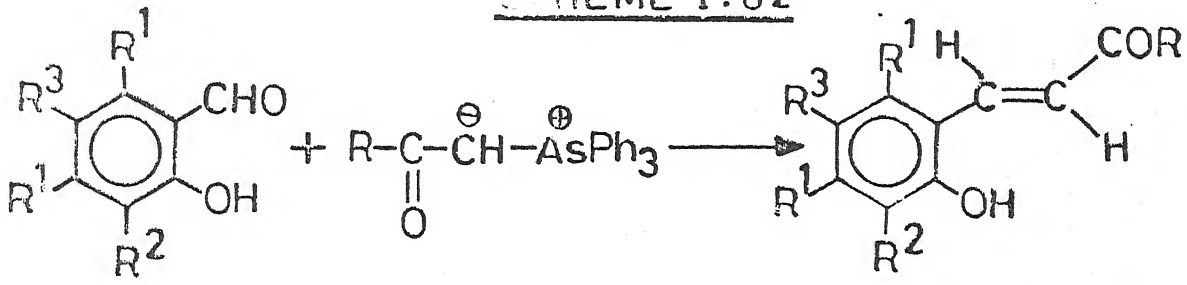
243 244 245

SCHEME I.81



246 247

SCHEME I.82



248 249 250

Like azomethine intermediates, arsorane (258) also gave 1:4 dihydro 1:2:4:5 tetrazines (260) when reacted with aromatic diazonium salts (259)[221] (Scheme I.85).

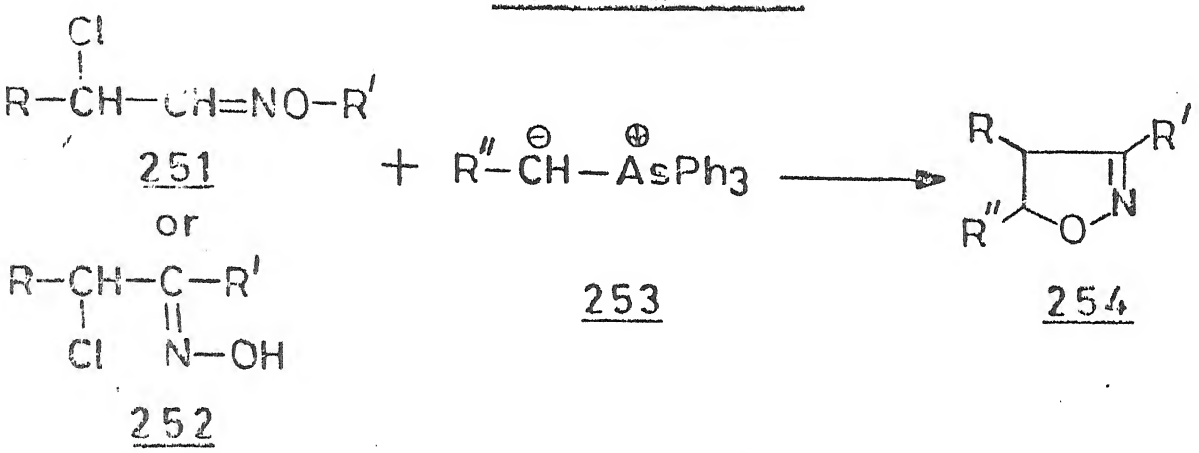
I.C. AZOMETHINE INTERMEDIATES (PYRIDINIUM YLIDS)

The development of the chemistry of nitrogen ylid intermediate (261) began with the early attemps to prepare organic derivatives containing pentavalent nitrogen . To this purpose, Schlenk and Holtz [222] created tetramethylammonium chloride with sodium triphenylmethylide (262) and isolated a red product, insoluble in organic solvents, to which they assigned strucure (263) (Scheme I.86).

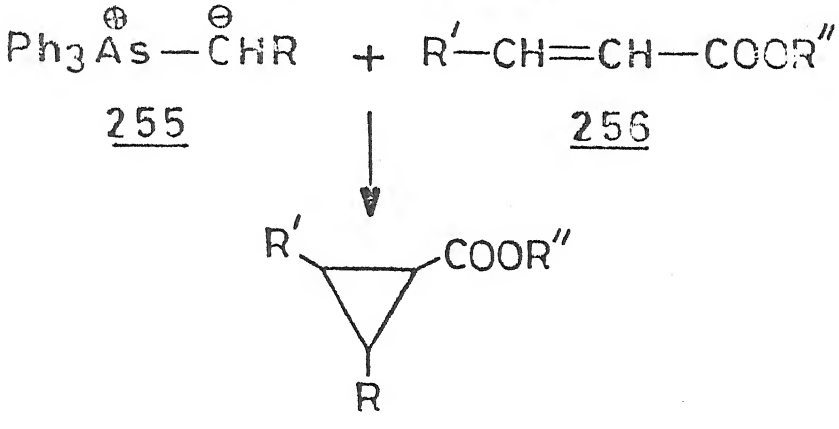
Later, Hager and Marvel[223] attempted to prepare analogous compounds, in which all the five groups around nitrogen were equivalent. These workers found that the reaction of triethyl-benzylammonium bromide with ethyllithium did not produced tetra-ethylammoniumbenzylid ruling out the existance of any intermediate in which all the five groups bound to the nitrogen atoms approached equivalency . From this observation Hager and Marvel [223] concluded that the material prepared by Schlenk and Holtz was tetralkylammonium salt of relatively stable triphenylmethyl carbanion (263) rather than the derivatives of pentavalent nitrogen.

In 1944 Wittig and Felletschin [224] began reinvestigation of the pentavalent nitrogen problem and succeeded in isolating a red powder from the treatment of 9-fluorenylidenetrimethyl-

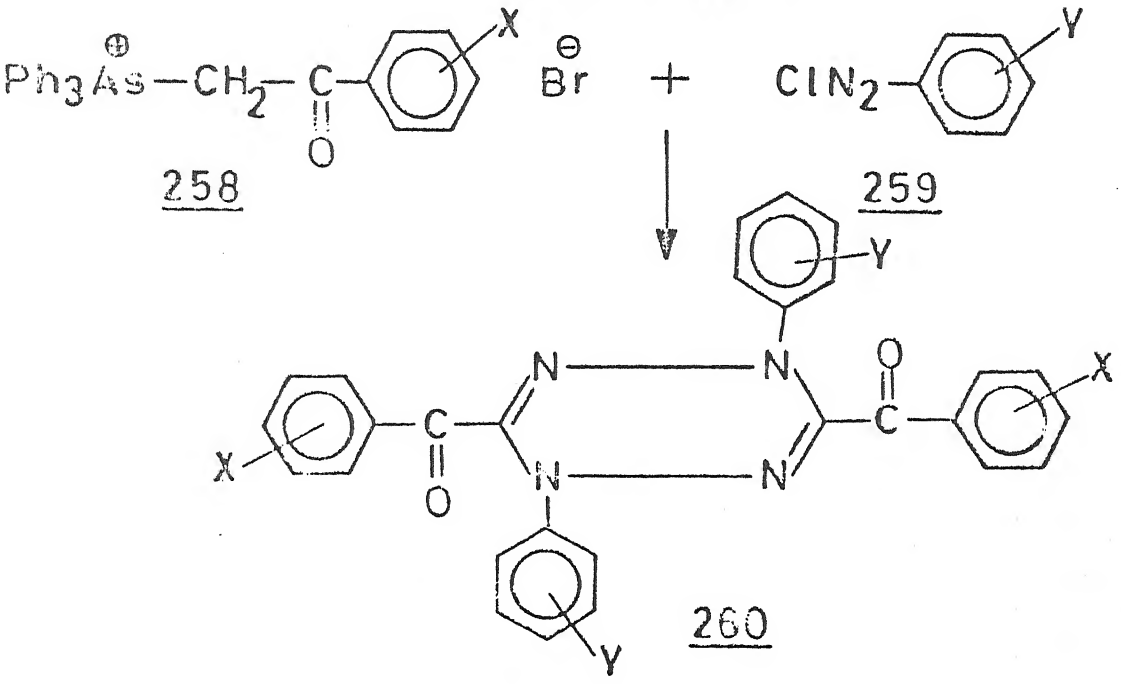
SCHEME I.83



SCHEME I.84



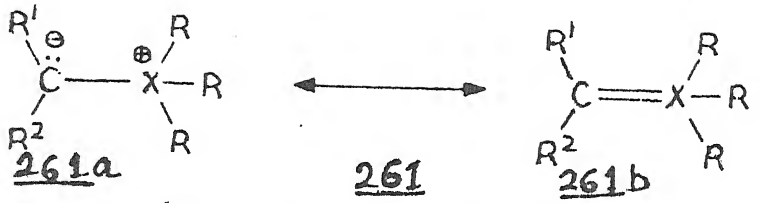
SCHEME I.85



ammonium bromide (264) with phenyllithium in ether. However,since benzene was isolated from the mixture, the compound could not be pentavalent nitrogen derivative and was assigned an ylid intermediate structure on the basis of its reaction with water, methyl iodide, iodine and benzyl bromide (Scheme I.87). Following this initial preparation of a stable material having an ylid intermediate structure, a variety of nitrogen ylid intermediates have been prepared, characterized and their chemistry has been reviewed .

The nitrogen ylid intermediates were grouped under many heads according to onium group structure which are :ammonium ylids (264), cycloammonium ylids (266), immonium ylids (267), cycloimmonium ylids (268), nitrile ylids (269) and diazonium ylids (270). The cycloimmonium ylids may be further divided into five membered cycloimmonium ylids and the six membered cycloimmonium ylids which includes azomethine and benzoazomethine intermediate.

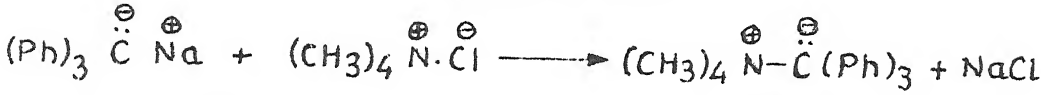
The stability of azomethine inermediate may be attributed to an extensive delocalization of positive charge on the pyridine ring as represented by various contributing structures (273a-d) (Scheme I.88) and to the carbanion participation in the resonance of heteroaromatic ring (274a-c) (Scheme I.89). The coulombic interactions, which are also responsible for the stability of some ammonium ylids, are less important in the case of azomethine intermediates so far as the stability is concerned and if it is assumed that there is only an electrostatic interaction between



261a ⟷ 261 ⟷ 261b

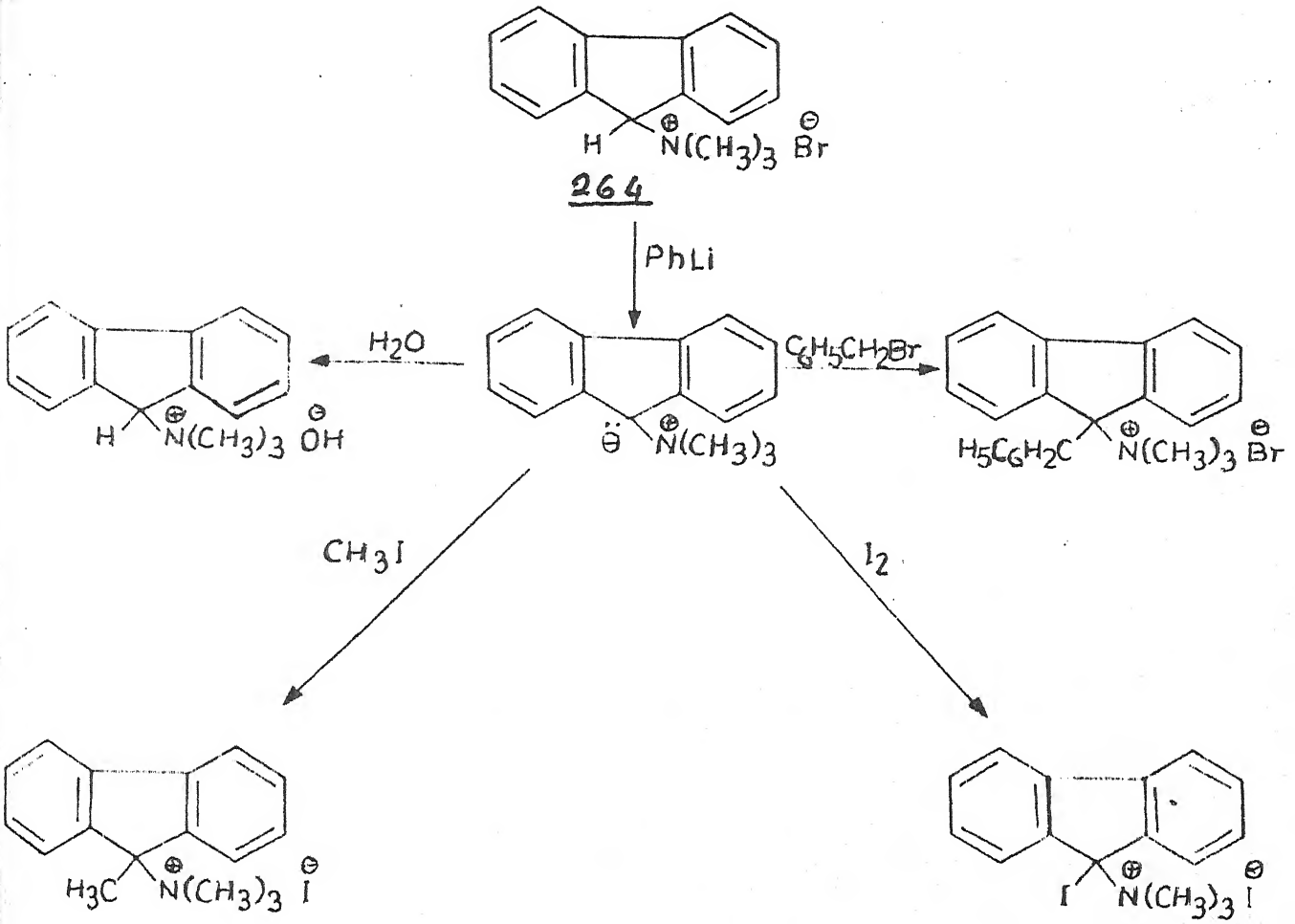
(where X may be N, P, As, S etc.)

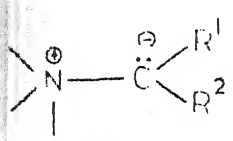
Scheme I.86



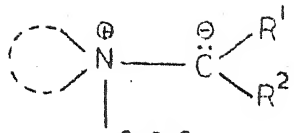
262 263

Scheme I.87

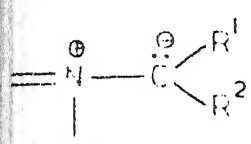




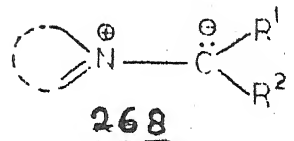
265



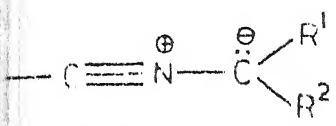
266



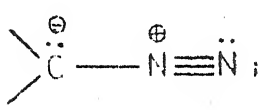
267



268

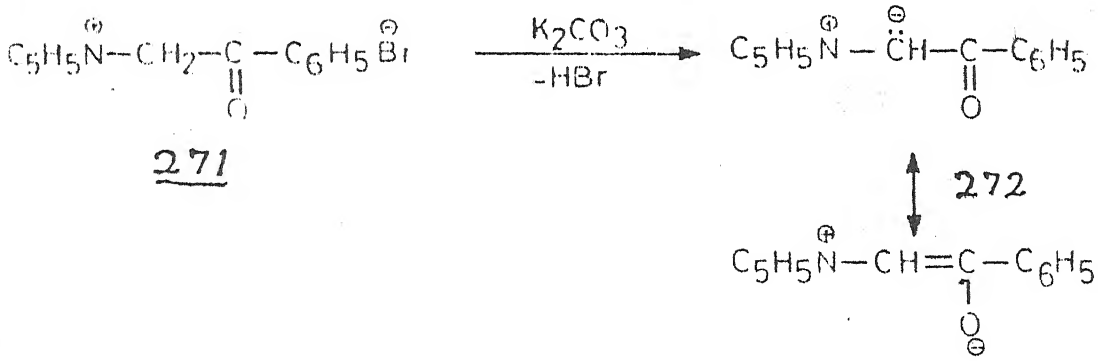


269

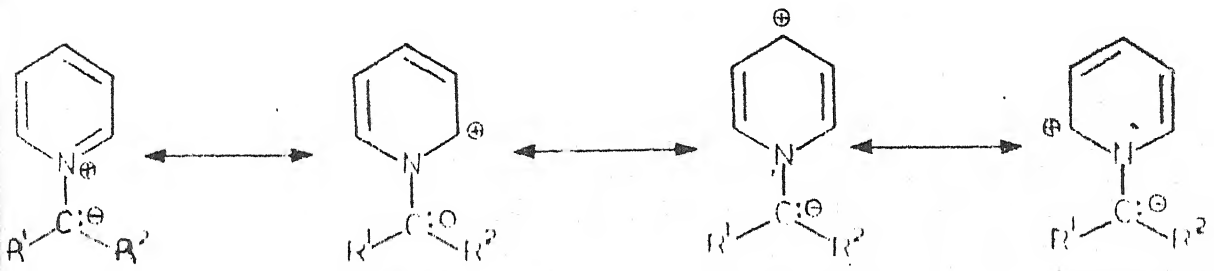


270

Scheme I.88



271



273a 273b 273c 273d

the carbanion and the onium group, as represented in the stucture (274b), the electron pair of sp^3 hybridized ylidic carbanion would be involved in a π d type of molecular orbital with the sp^2 hybridized nitrogen atom of pyridine ring. However, overlaping is more effective, if we considered the resonating form (274c) in which there is an interaction of the bielectronic p-orbital with the π-electron of the pyridine ring and azomethine intermediates afford stability [11] . The stability has been found to be influenced by the nature of substituents R^1 and R^2 attached to the ylid carbanion. If these groups are electron withdrawing, additional resonance structures occur determinig a marked sp^2 hybridization of the ylid carbon through charge delocalization.[11]

I.C.1 PREPARATION OF AZOMETHINE INTERMEDIATES (PYRIDINIUM YLIDS)

C.1.1 Azomethine from pyridinium salt (salt method)

The most common method used for the preparation of azomethine intermediate involves the quaternization of substituted alkylhalides with respective tetiary bases viz pyridine the picolines, quinoline and isoquinoline which in the second step loses an hydracid molecule in basic media and is converted to respective intermediates (277)[225,226] from its substituted alkyl pyridinium halides (276) (Scheme I.90). Quaternization may also be performed by the treatment of tertiary

base with an active methylene derivative and iodine. This method, first reported by Ortoleva [227-228] and widely applied in a great number of cases by KIng [229-231] and others [232], known as king Ortoleva method and results in the formation of the salt of type (278)[233] (Scheme I.91)

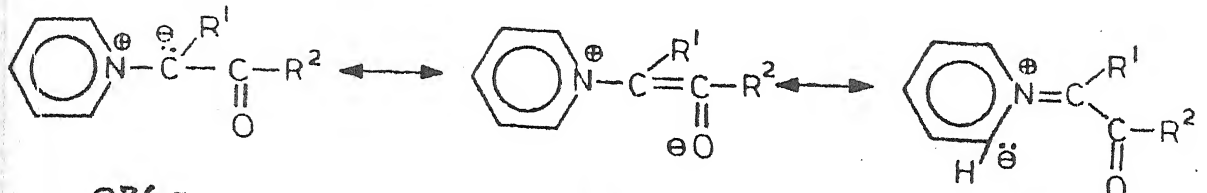
The strength of base necessary for dehydrohalogenation of the corresponding salt depends on the acidity of α —hydrogen atom. Most common bases used for this purpose are aqueous solution of alkali carbonates [232] or solution of amines in anhydrous aprotic solvents. Sometimes, the use of sodium hydride in dimethylformamide has founed to be advantageous, particularly for unisolable azomethine intermediates which are to be used in subsequent reactions .[234,235] A wide number of azomethine intermediates are incapable of being isolated due to their sensitivity towards atmospheric components and, therefor, generated in anhydrous media under inert atmosphere and used as such in subsequent reactions.[234]

C.1.2. Azomethine Intermediates from azaheterocycles and ethylene oxide

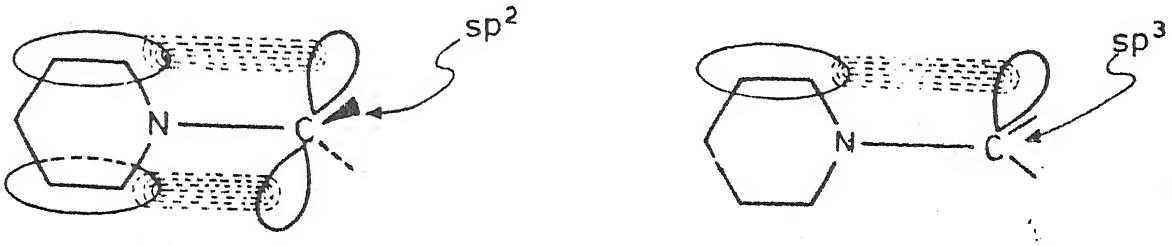
Linn et al.[237] and others [238] have reported the formation of many dicyanomethylides (281) which are highly stable, by the reaction of tetracyanoethylene oxide (280) with azaheterocycles at 0°c (Scheme I.92)

C.1.3. Azomethine Intermediates from diazo compounds

Scheme 1.89

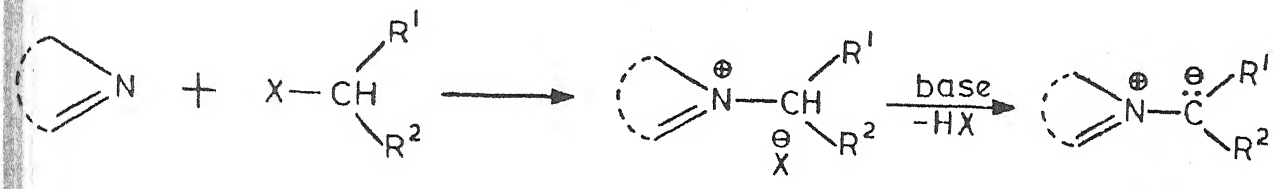


274a 274b 274c



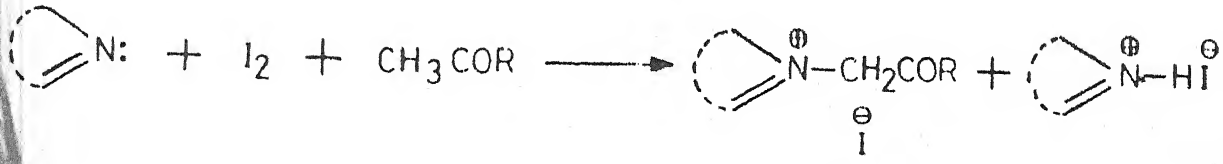
275a 275b

Scheme 1.90



276 277

Scheme 1.91



278

Azomethine intermediates (283) have also been prepared by the irradiation of triphenyl or tetraphenyldiazocyclopentadiene (282) in pyridine under nitrogen with a high pressure of mercury lamp through a pyrex filter [239] (Scheme I.93)

C.1.4. Azomethine Intermediates from N-heterocycles and Carbene

Azometine and benzoazomethine intermediates (285) have also been formed by the reaction of carbene (284) on azaheterocycles [240] (Scheme I.94).

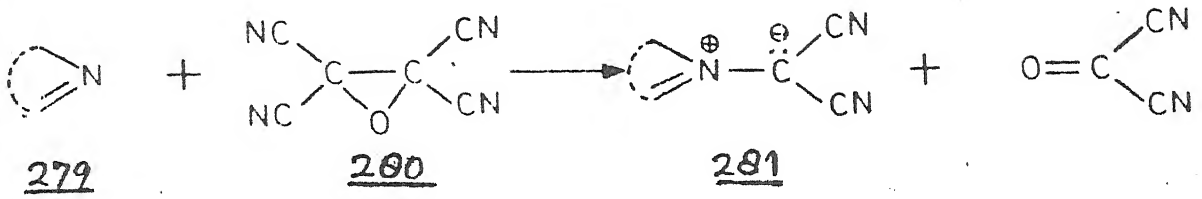
C.1.5. Synthesis of disubstituted azomethine intermediates

Disubstituted azomethine intermediates (287,288) have been synthesized from monosubstituted azomethine intermediate (286) directly by treatment with acylating reagent,[241] isocyanates [242,236] and thiocyanates [243,244] (Scheme I.95).

Recently, Leonte and Zugravescu [243] have synthesized dicynopyridiummethylid (290) by heating cyanocarbamoylpyridiniummethylid (289) with $POCl_3$ in the presence of sodium pyrosulfite. But when acetic anhydride was used as dehydrating agent instead of $POCl_3$, cyanoacetylpyridiniummethylid (291) was formed. The ylid intermediate (291) was also prepared by acetylation of the ylid (292) . Alternatively, ylid (290) could be synthesized by the reaction of bromocyanoacetic ester (293) with carbalkoxypyridium ylid (294) (Scheme I.96).

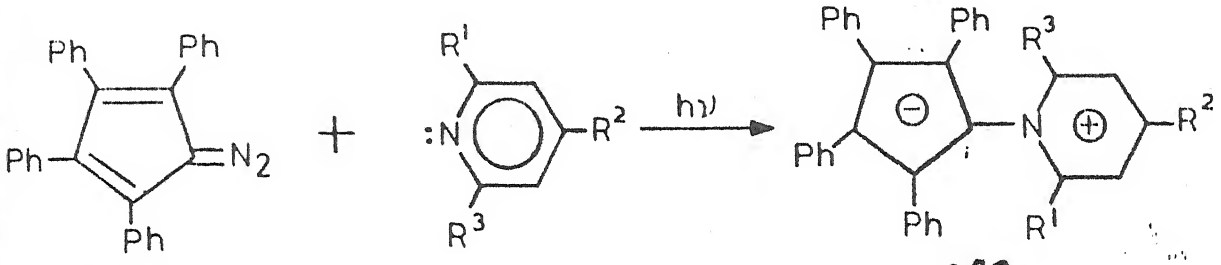
I.C.2. REACTIONS OF AZOMETHINE INTERMEDIATES (PYRIDINIUM YLIDS)

Scheme I.92



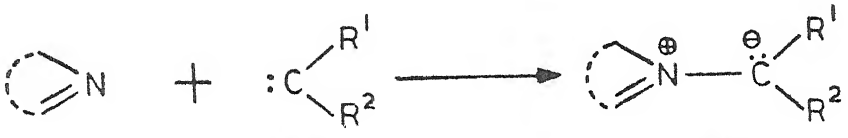
279 280 281

Scheme I.93



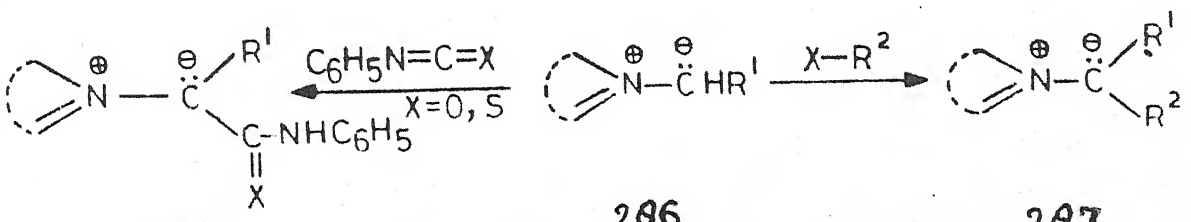
282 283

Scheme I.94



284 285

Scheme I.95



288 286 287

C.2.1. Thermolysis

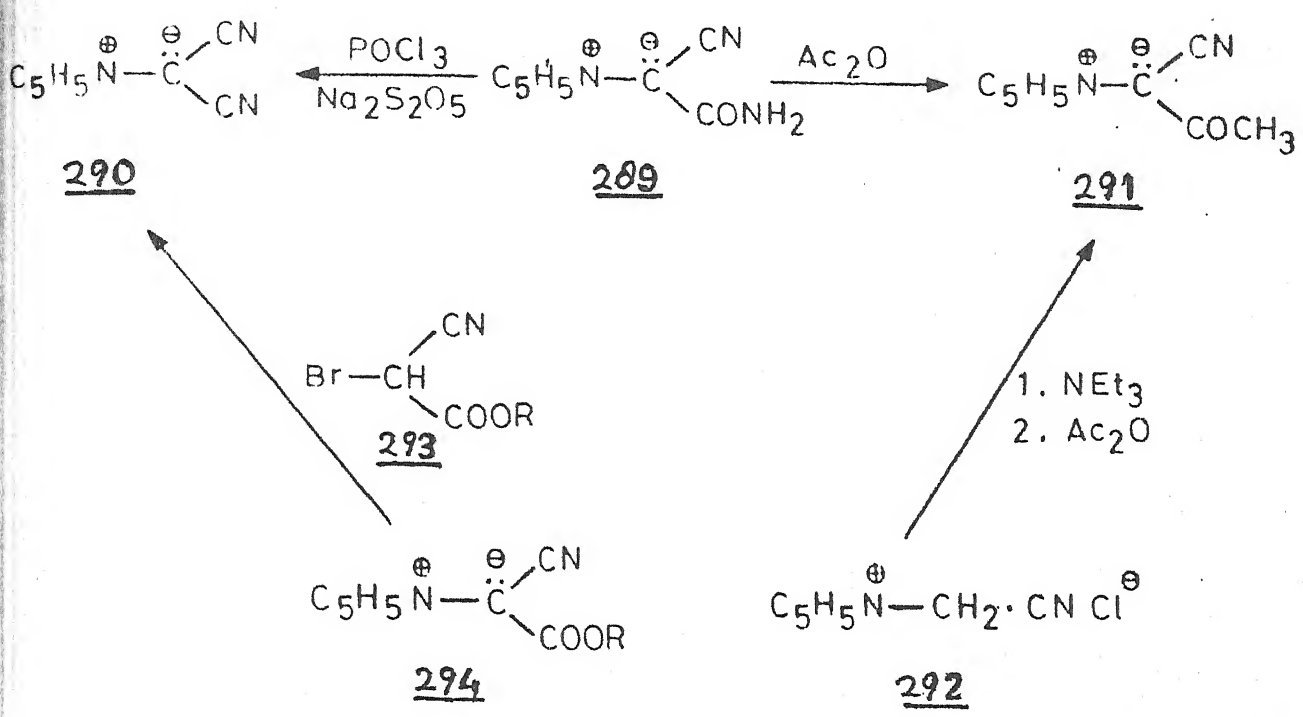
The thermal stability of azomethine intermediate was not studied in adequate experimental conditions. However, Cook et al.[244] isolated dibenzoylethylene (295) by sublimation of the azomethine intermediate (293) at 150°C in high vacuo conditions. The former product seemed to have been resulted from dimerization of carbene intermediate (294), formed by the heterolytic cleavage of ylidic bond (Scheme I.97). The thermolysis[234] of the azomethine intermediate (296) in benzene in the presence of copper or copper oxide afforded 1,3-dibenzoylindolizine (297). The mechanism of this reaction is still obscure (Scheme I.98). Recently, Katritzky et al. [245] have studied the thermolysis of ter-butylcarboxymethylpyridinium salt which afforded different pyridium salts - 1-carboxymethyl and 1-methylpyridium salts.

Zugravescu et al. [246] have studied the thermal decomposition of mono- and disubstituted isoquinolinium ylid (298) and reported the formation of isoquinoline and cyclopropane derivatives (300), formed by trimerization of carbene intermediate (299) (Scheme I.99).

C.2.2. Photolysis of azomethine intermediates[248,247]

The photoreaction of disubstituted methylid (301) in diluted benzene are of two types : (i) The cleavage of C$^-$ – N$^+$ ylid bond with formation of the heterocycle and the disubstituted carbene. This is usually the main reaction ; (ii) the photoisomerization of azomethine intermediates which involve the contraction or

Scheme 1.96

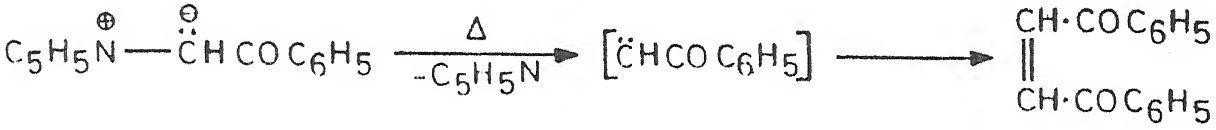


290 289 291

293

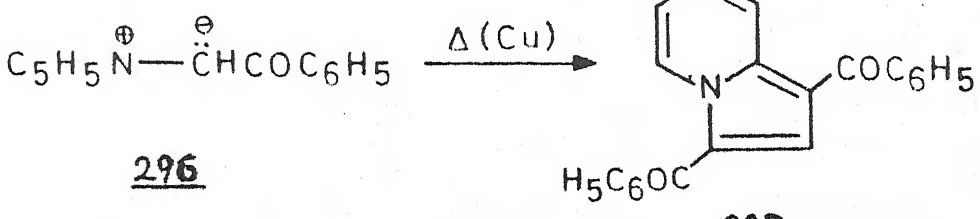
294 292

Scheme 1.97



295

Scheme 1.98



296 297

expansion of the heterolytic ring (Scheme I.100).

C.2.3. Alkylation

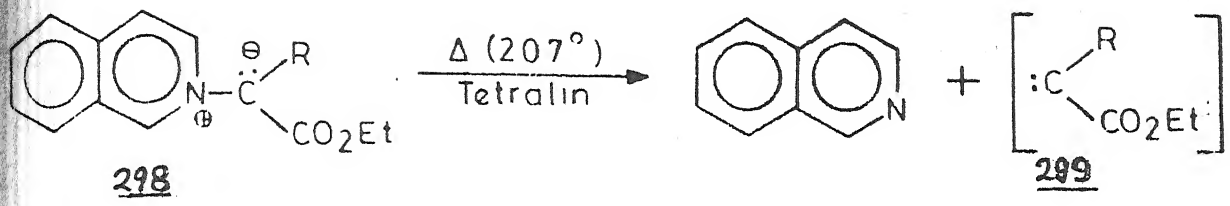
Azomethine intermediates having active methylene group, are capable of undergoing substitution reaction with alkyl halides to affored carbanion disubstituted ylids (302) presumabely via intermediacy of salt (304) which in presence of base loses hydroacid molecule and converted into ylid (305)[247] (Scheme I.101) . However with an alkyl group generally reduces the compounds stability .

If alkylation is carried out without using any dehydrohalogenating agent, a series of products are obtained. It was observed that benzopyridinium methylid (306) with phenacylbromide yields several products with different structures (307-311), owing to the possible interaction between the intermediate and the ylid, and to the transylidation and bond cleavage (Scheme I.102) . Henrick et al.[234] reported the preparation of a wide range of ketones (314) by the reduction of the salt (313) with zinc and acetic acid formed by the alkylation of ylid (312) (Scheme I.103).

C.2.4. Acylation

Azomethine intermediates, due to strong nucleophiliicity of the ylid carbanion, can be acylated easily by a suitable acylating agent (Scheme I.104) . However, the course of reaction varies with the nature of acylating agent used. Thus, pyridinium

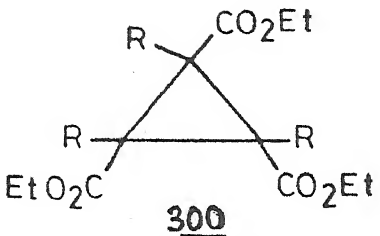
Scheme I.99



298 299

R = H, -CO2Et

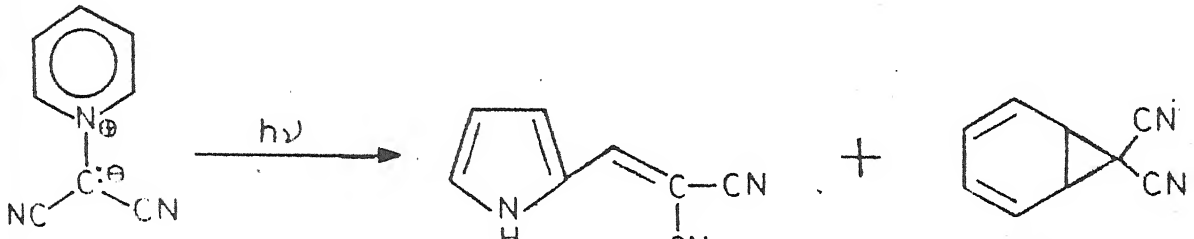
3(39) ⟶



300

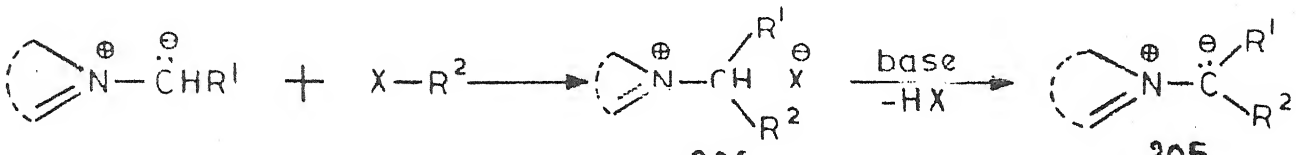
R = H, -CO2Et

Scheme I.100



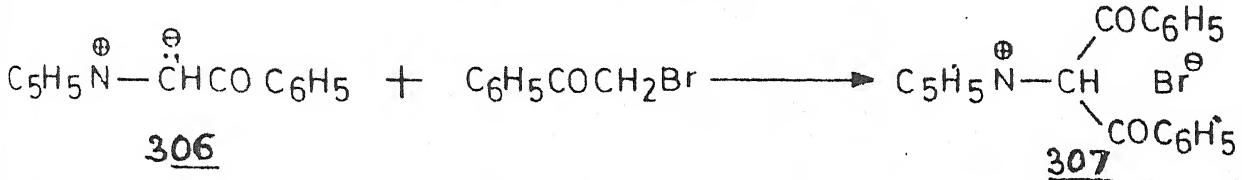
301 302 303

Scheme I.101

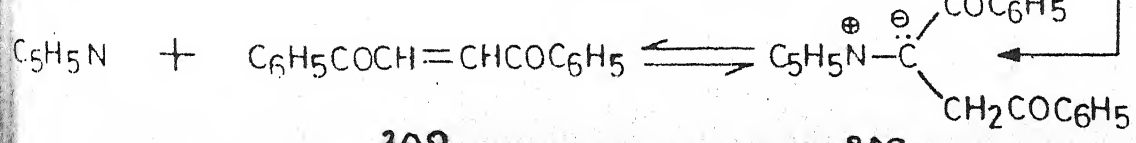


304 305

Scheme I.102



306 307



309 308

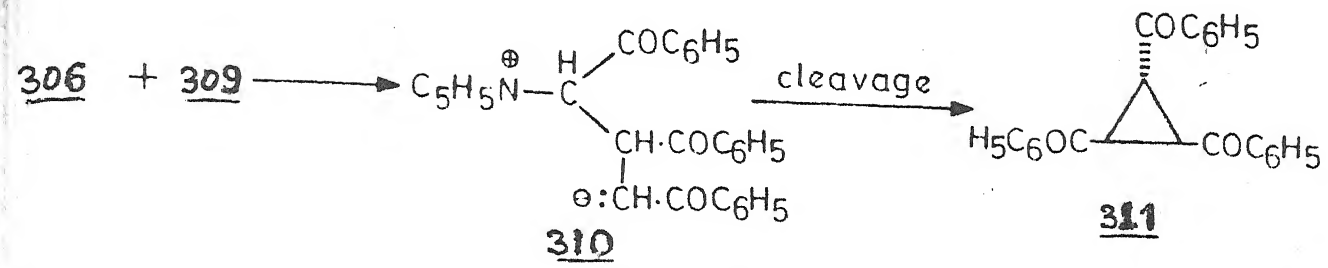
phenacylid (315) with benzoylchloride led to the O-acylated (317) and s-acylated products (318)[250] (Scheme I.105) whereas acylation with benzoic anhydride affords c-acylated products only .[234,235] Similarly, the interaction of benzoic anhydride with isoquinolinium ylids (316) affords c-acylated products[251,252] (320) only (Scheme I.106)

C.2.5 Arylation

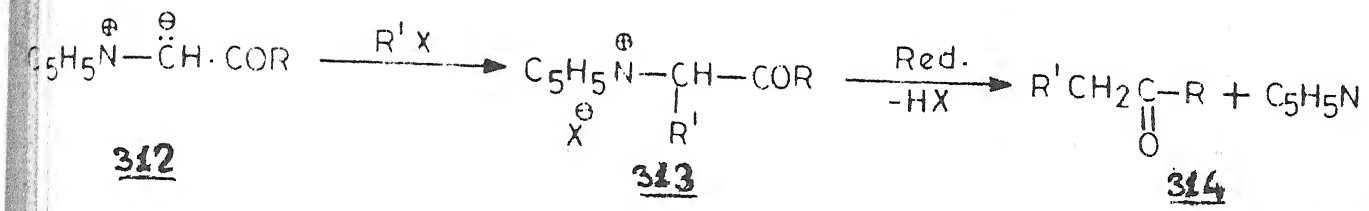
Similar to the alkylation reaction arylation in azomethine intermediate is comparatively difficult due to diminished reactivty of aryl halides. Reuschling and Krohnke [253] reported that quinolinium phenacylide generated 'in situ' from the corresponding quaternary bromide, forms with picrylchloride (323),a red product to which structure (325) was assigned which actually forms via intermediacy of (324). The compound (325) by treating with concentrated sulphuric acid, loses the benzoyl group resulting in 8,10-dinitrosoindolo (2,1-a) quinoline (326) (Scheme I.107).

Similary, pyridininium and isoquinolinium benzoylmethylid (327 a,b) reacted 'in situ' with picrylchloride in alkaline medium afforded deep colour products to which structure (328 a,b) were assigned . In presence of organic bases viz piperidine, the compound (328 a,b) eliminates nitrous acid forming 8-benzoyl-9,11- dinitrodibenzo (9 a) indolizines (329 a,b) (Scheme I.108).

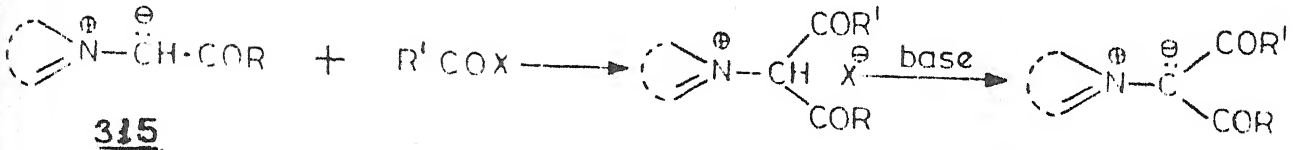
Scheme I.102 (contd)



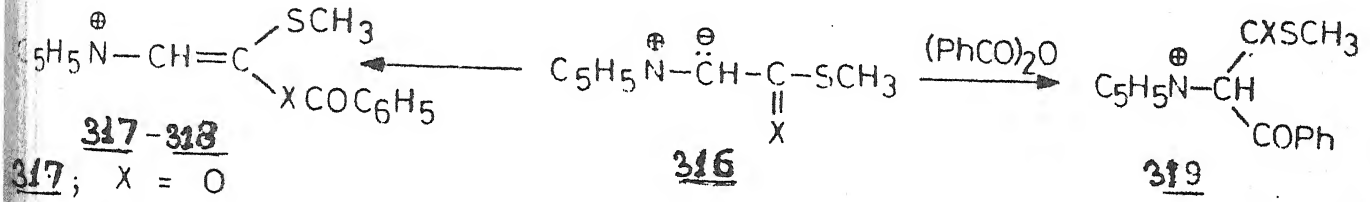
Scheme I.103



Scheme I.104



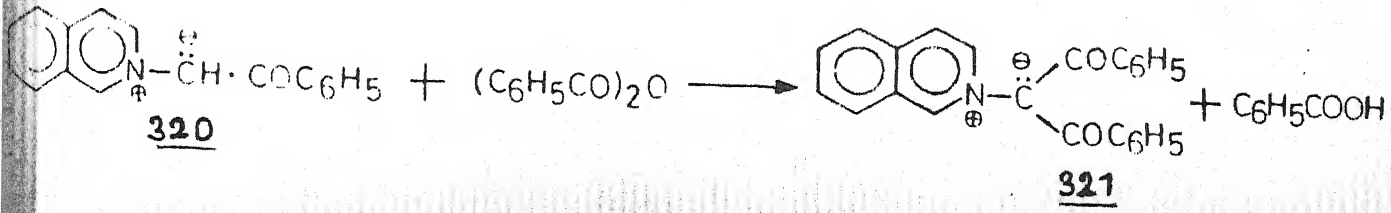
Scheme I.105



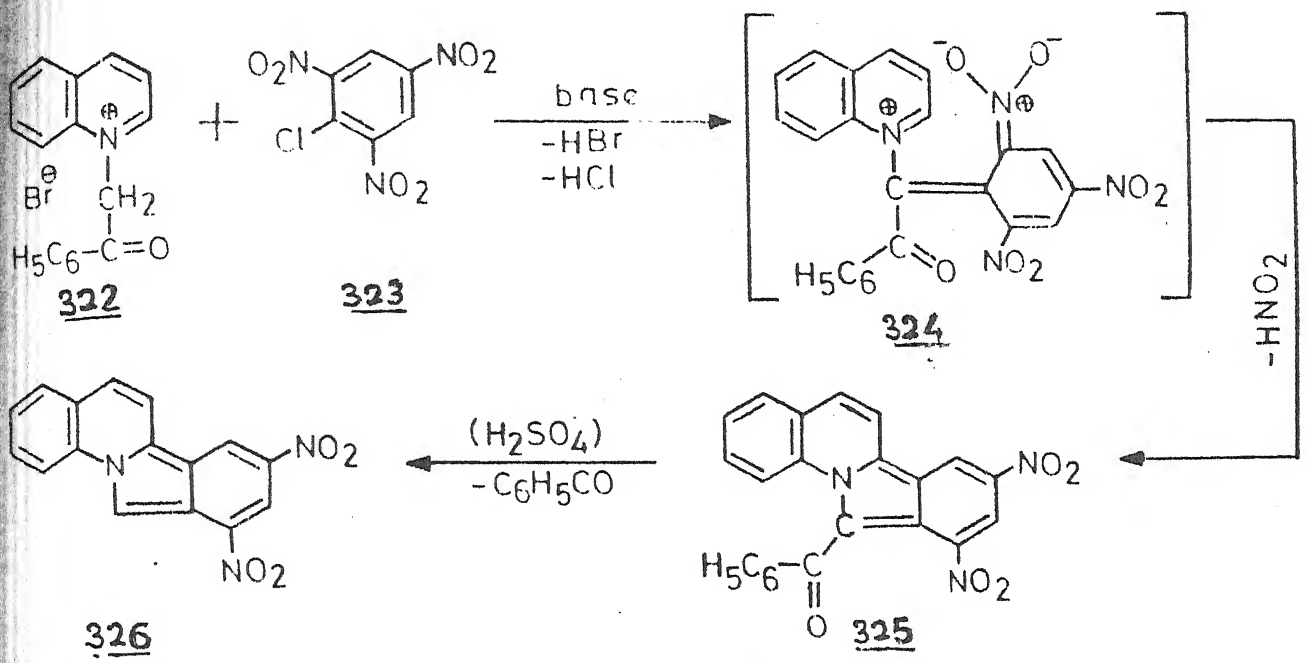
317; X = O

318; X = S

Scheme I.106

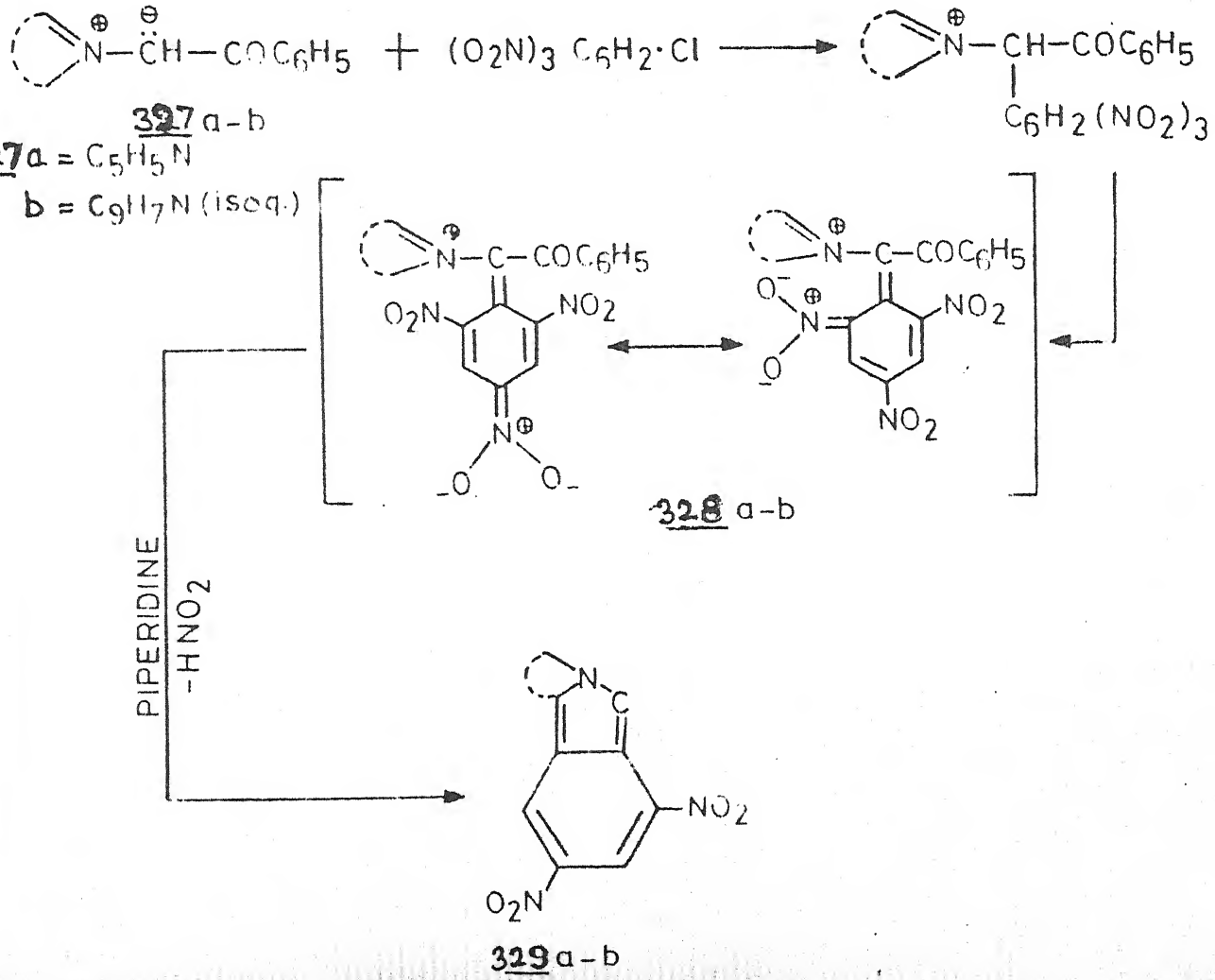


Scheme 1.107



322 323 324 325 326

Scheme 1.108



327 a-b

327 a = C_5H_5N

b = C_9H_7N (isoq.)

328 a-b

329 a-b

C.2.6. Reaction with aldehydes

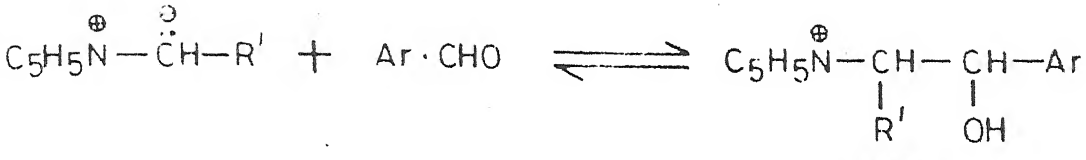
Azomethine intermediates react with aldehydes to afford aldol type products as a pyridinium ethanolic salts (330)[254-256] (Scheme I.109) . Howe and Ratts reported the deuterinium exchange studies in the piperidine catalyzed condensation of N-methylpyridinium iodide (331) with aromatic aldehyde and observed along with the formation of N-(2-hydroxy-2-phenylethyl) pyridinium halide (333), 2-(∝-hydroxybenzyl)-1-methylpyrdinium halide (332) is also formed via N-ylid (Scheme I.110).

Azomethine intermediate generated from pyridinium salt (334) in which substituent R is a strong electron withdrawing group, reacts well with aromatic aldehyde in presence of pyridine to afford vinyl pyridinium salt (335)[257] (Scheme I.111).

Azomethine intermediates when treated with aromatic aldehydes in presence of ammonia undergo Mannich type condensation to afford pyrimidines. Thus N-phenacylazomethine intermediate (236) reacts in glacial acetic acid with ammonia and aromatic aldehyde carrying electron attracting group to afford triarylpyrimidine (337)[256] (Scheme I.112)

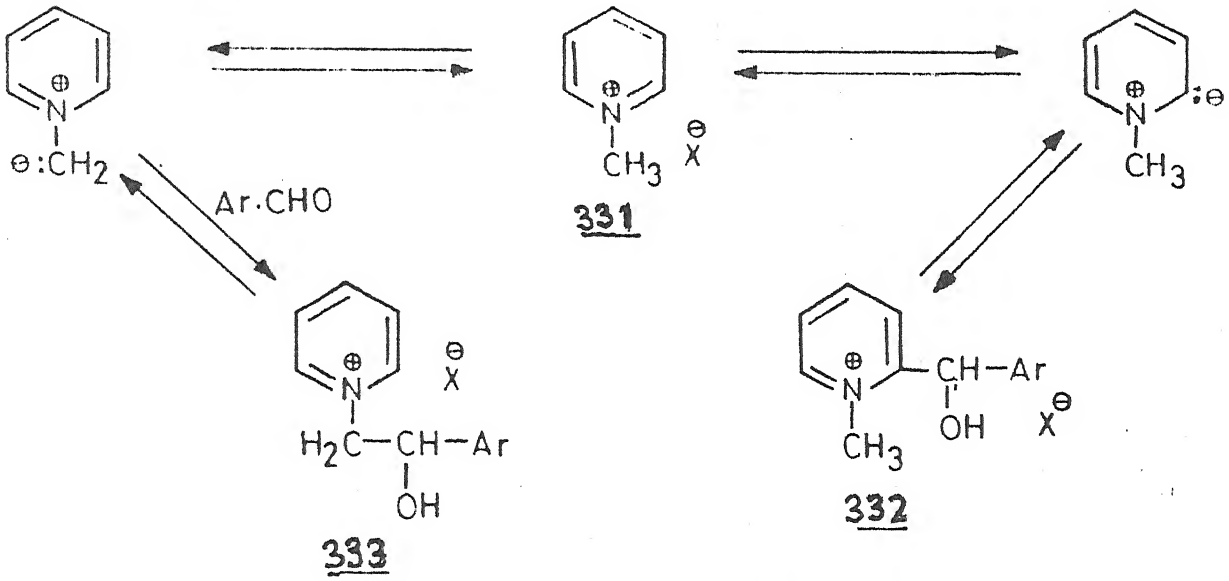
However , the semistabilized isoquinolium ylids (338) on reaction with aromatic aldehydes in presence of suitable base forms corresponding ethanols (340) via intermediacy of compound (339) (Scheme I.113).

Scheme I.109



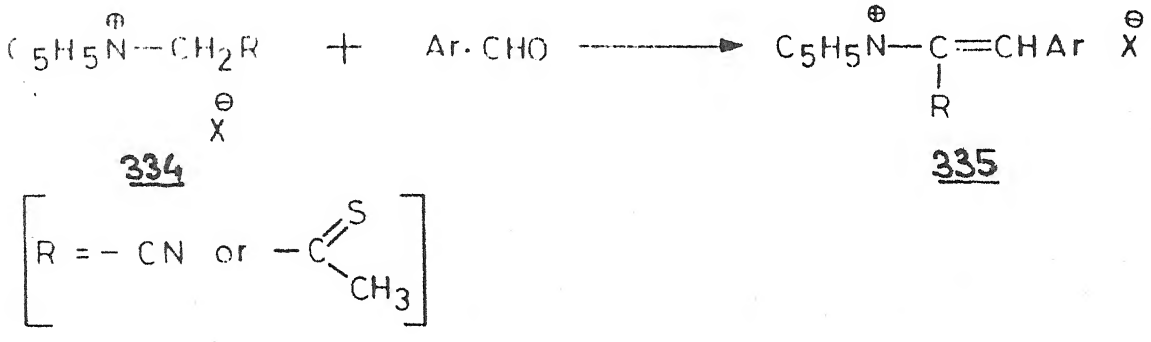
330

Scheme I.110



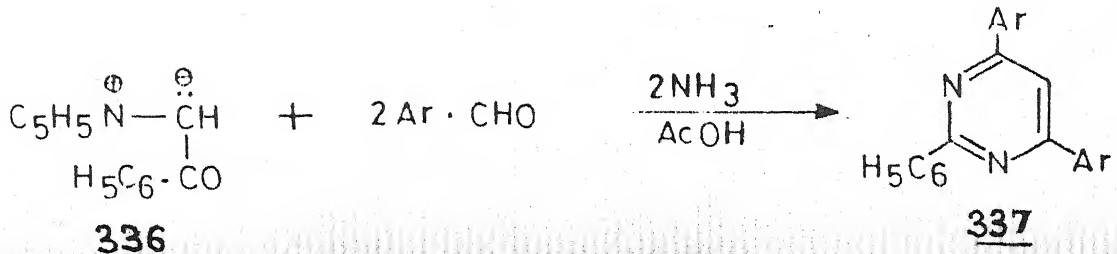
331 332 333

Scheme I.111



334 335

Scheme I.112



336 337

C.2.7. Reaction with Ketones

Not only aldehydes, but ketones are also capable of undergoing reaction with the azomethine intermediates .However, mode of the reaction depends upon the nature of ketones employed for the purpose. Thus, phenacyclidene azomethine intermediate (341) react with tropone to afford 2-hydroxy-2-phenyl-3-phenacyl-2H-cyclohepta (b) furan[258](342) (scheme I.114).

Contrary to this, azomethine intermediates may take a different course when they are made to react with 1,2-diketones. This approach was proved to be highly indispansable in the synthesis of heterocycles. Noteworthy, in this respect, is the synthesis of 2,3-disubstituated dehydroquionolizium salt (344) through the condensation of 2-picolinium salt (343), carrying activated N-pyridinoylmethyl group, with 1,2-diketone in the presence of weak base [256] (Scheme I.115). This reaction in the later stage proved to be highly useful for the comprehensive synthesis of quinolizine ring [259] particularly useful in building up of alkaloid nucleus. Azomethine intermediates were also found to undergo reaction with quinones, resulting in the formation of heterocyclics which in turn, depends upon the cyclization agent. For example, N-phenacylpyridinium ylid reacts with 2-chloro-1,4-napthaquinone following Michael type of addition,to afford stable substituted phenacyl naphthaquinone (345) which on cyclization with zinc and acetic acid gives benzocoumarine (346). However, benzocinnoline (347) is the exclusive product of the reaction

when hydrazine hydrate is employed for bringing about aza ring closuer of the intermediate product (345)[260,261] (Scheme I.116).

C.2.8. Reaction with α,β-unsaturated ketones

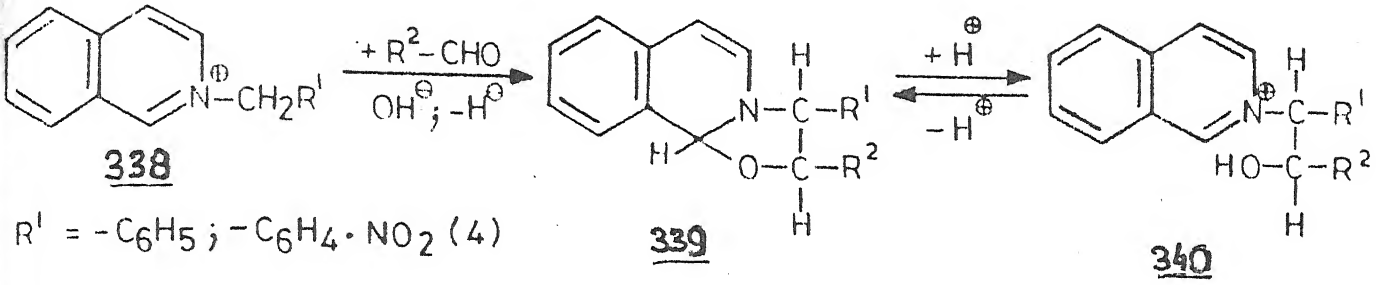
Azomethine and isoquinolinium ylids react with α,β-unsaturated ketones in a variety of ways depending upon the stucture of ylid and experimental conditions . Thus aroylmethylene azomethine intermediates and their isoquinolinium counterparts (348 a,b) readily add on α,β — unsaturated carbonyl compounds to undergo Michael addition affording 1,5-dionylpyridinium and 1,5-dionylisoquinolinium derivatives (349 a,b) which on treatment with a mixture of glacial acetic acid and ammonium acetate used as cyclization agent, give 2,4,6-triarylsubstituted pyridines (350)[256,157,232] (Scheme I.117), whereas N-(amminoformylmethylene)-azomethine intermediates (351) with α,β-unsaturated ketones afford α-pyridones (352)[262] (Scheme I.118). Krohnke et al. have applied this method in the synthesis of a variety of useful pyridines and pyridones .

Pyridinium salts (353) with active methylene group, when reacted with substituted benzalacetophenones in presence of anhydrous zinc chloride, afforded polycyclic aromatic hydrocarbons (355)[256,263] (Scheme I.119).

C.2.9. Reaction with nitroso compounds

Azomethine and isoquinolinium ylids (356 a,b) react with nitrosobenzene to afford nitrone (357 a,b)[264,265] (Scheme I.120).

Scheme I.113



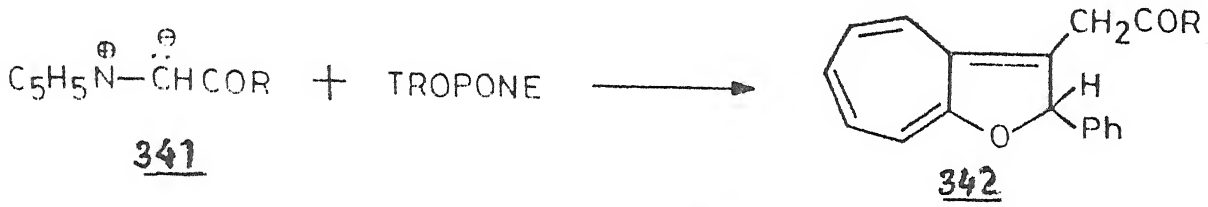
338

$R^1 = -C_6H_5 ; -C_6H_4 \cdot NO_2$ (4)

339

340

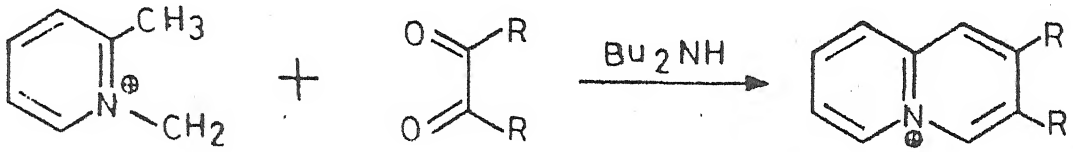
Scheme I.114



341

342

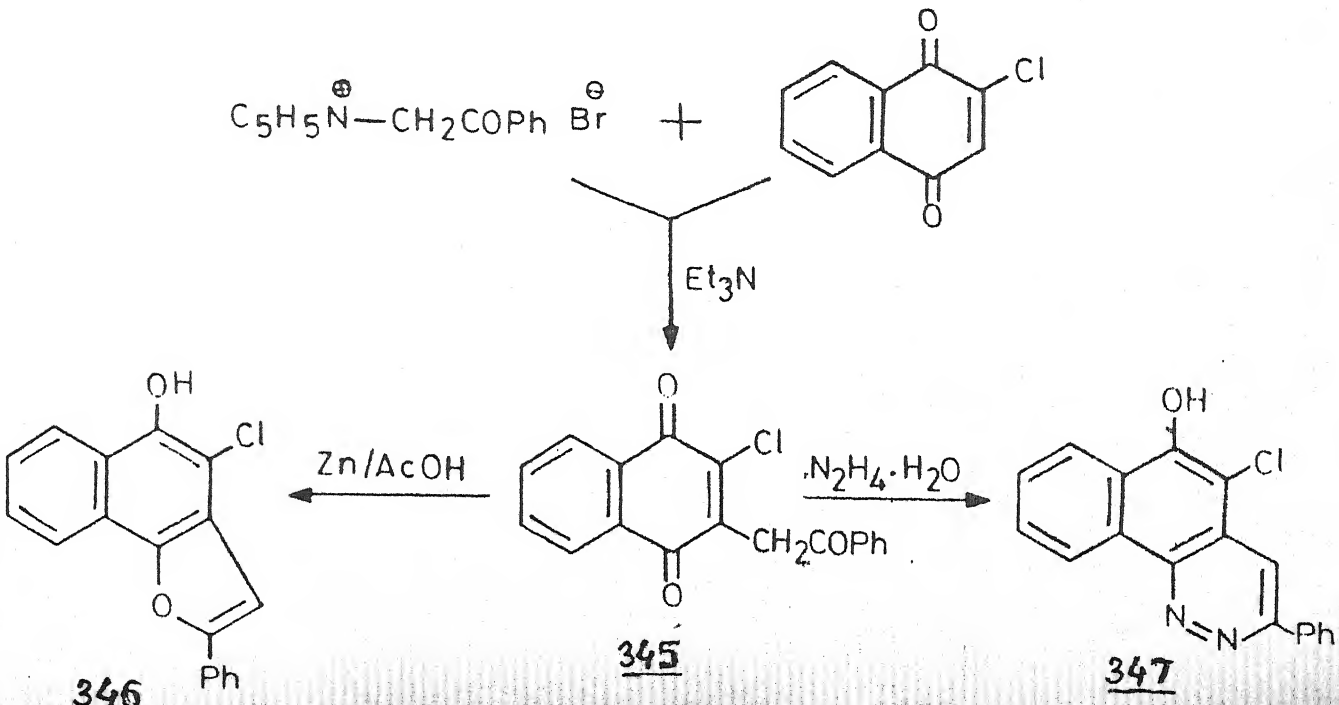
Scheme I.115



343

344

Scheme I.116

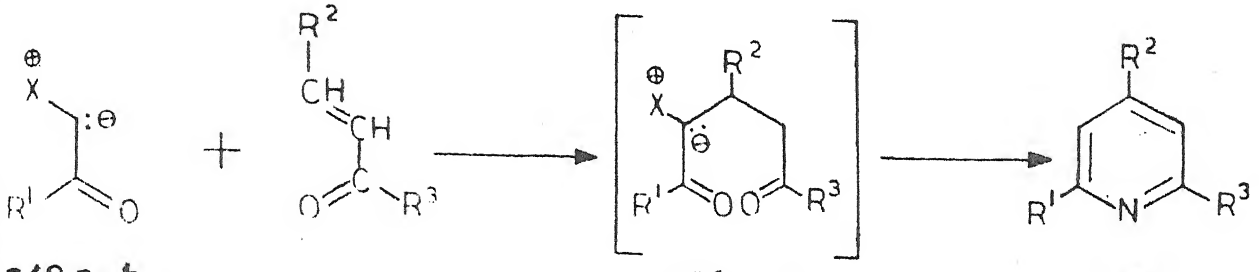


346

345

347

Scheme 1.117



348 a-b

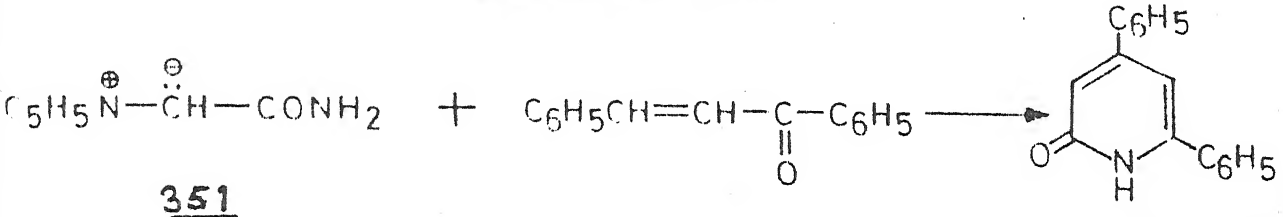
348 349 a X = C_5H_5N

b X = C_9H_7N

349 a-b

350

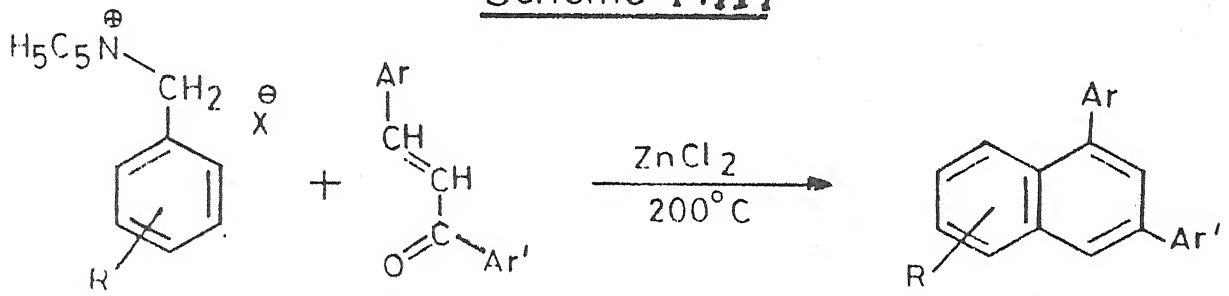
Scheme 1.118



351

352

Scheme 1.119

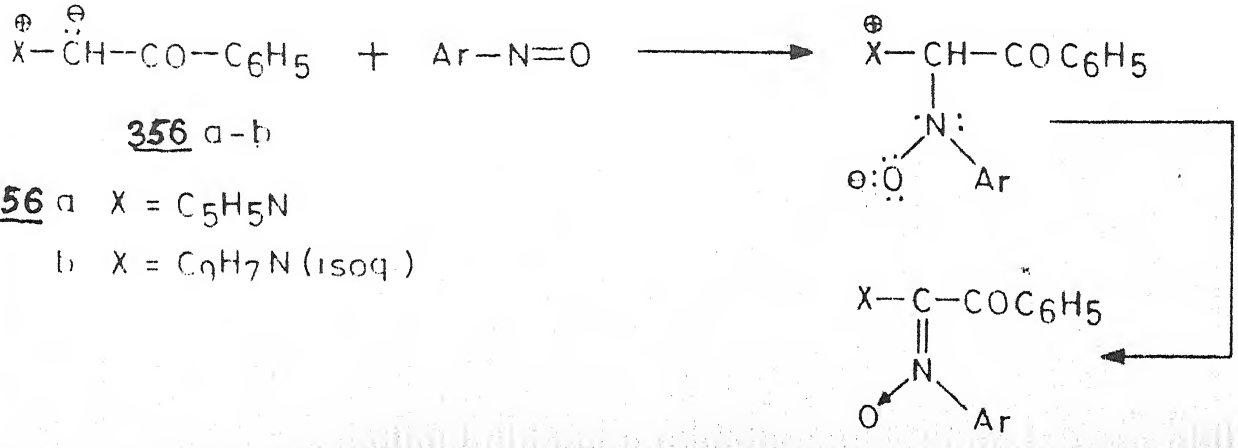


353

354

355

Scheme 1.120



356 a-b

356 a X = C_5H_5N

b X = C_9H_7N (isoq.)

357

Reactions of phenacylazomethine intermediate (358) with 1-nitroso-2-naphthol and 1-nitroso-2-naphthylamine were found to afford naphthoxazole derivatives (359) and benzoquinoxaline N-oxide derivatives (360)[266] (Scheme I.121).

C.2.10. Reaction with C=S bond

Phenacylazomethine intermediates (361) undergo addition with carbon disulfide to give sulfur containing betaine (362) which on reaction with alkyl halides gives S-alkylated products (363)[226,267] (Scheme I.122).

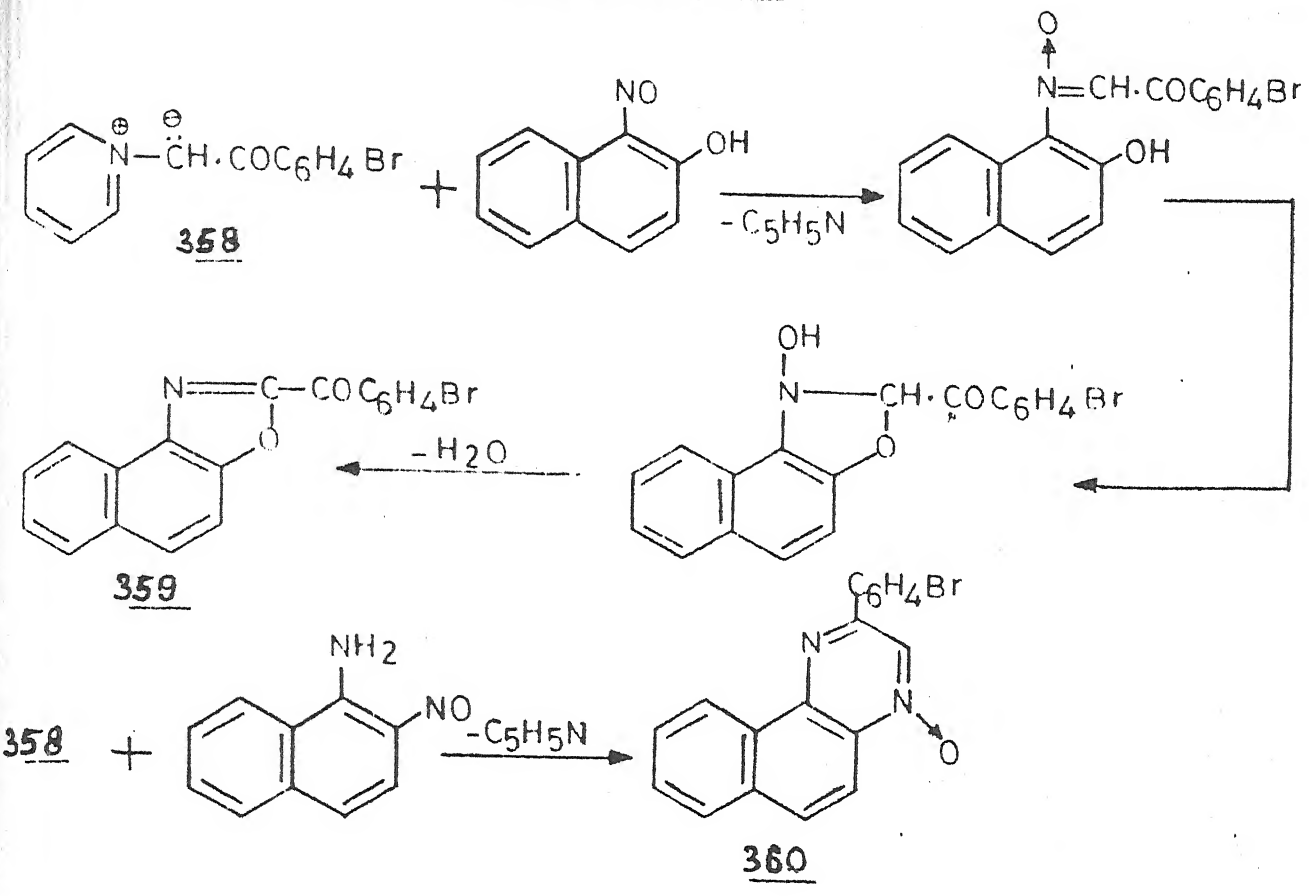
C.2.11. Reaction with isocyanates and isothiocyanates

Azomethine,isoquinolinium and phenanthridinium ylids due to strong nucleophilic character of the ylid carbanion afford carbon disubstituted ylids (365) on reaction with phenylisocyanate and phenylisothiocyanate via intermediacy of the betaine derivatives (364) [234,235] (Scheme I.123)

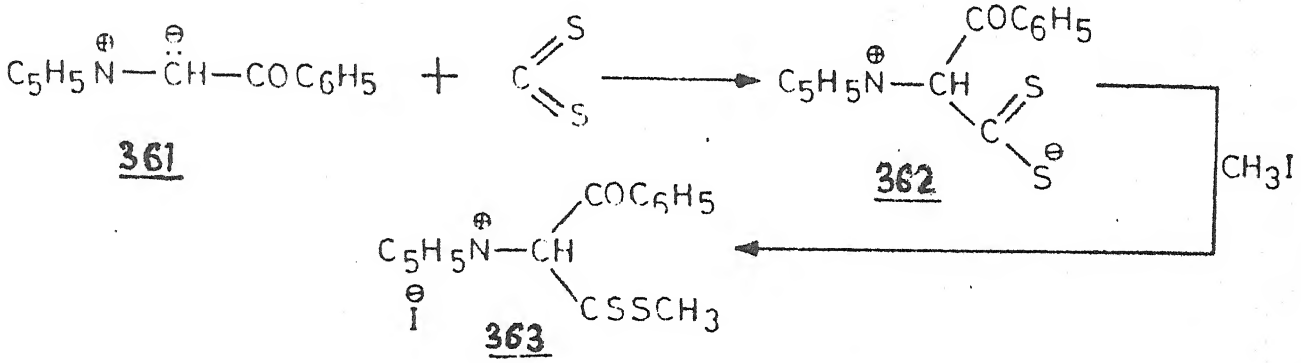
C.2.12 Reaction with nitrile imine

Pyridinium phenacylide generated 'in situ' with sodium ethoxide on reaction with nitrile imine in dioxane methanol media afforded the adduct[269] (366) but the same reactants differ when triethylamine and chloroform was used instead of sodium methoxide and dioxane-methanol and form a mixture of products (367) and (368) (Scheme I.124).

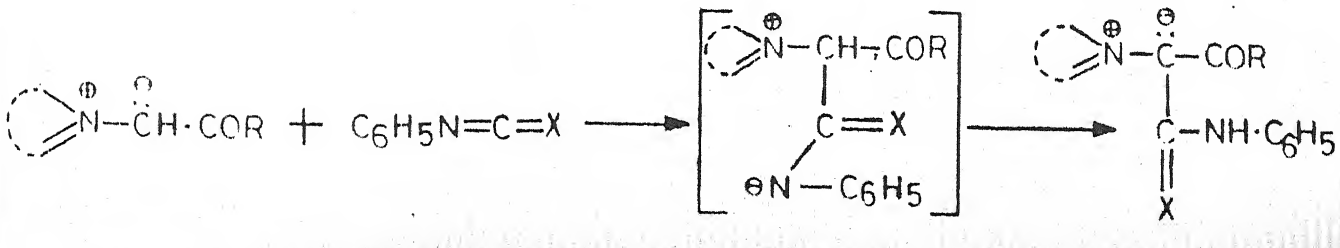
Scheme I.121



Scheme I.122



Scheme I.123



C.2.13. Reaction with nitromethane

kiel and krohnke[270] studied the cyclization reaction of isoquinolinium ylid (369a) generated 'in situ' from the respective precursors by using sodium carbonate as dehydrohalogenating agent and reported the formation of two products (373a) and (374) via intermediacy of (372) formed by dehydration of another intermediate(371) formed by the internal aldolization of primary reaction product (370).

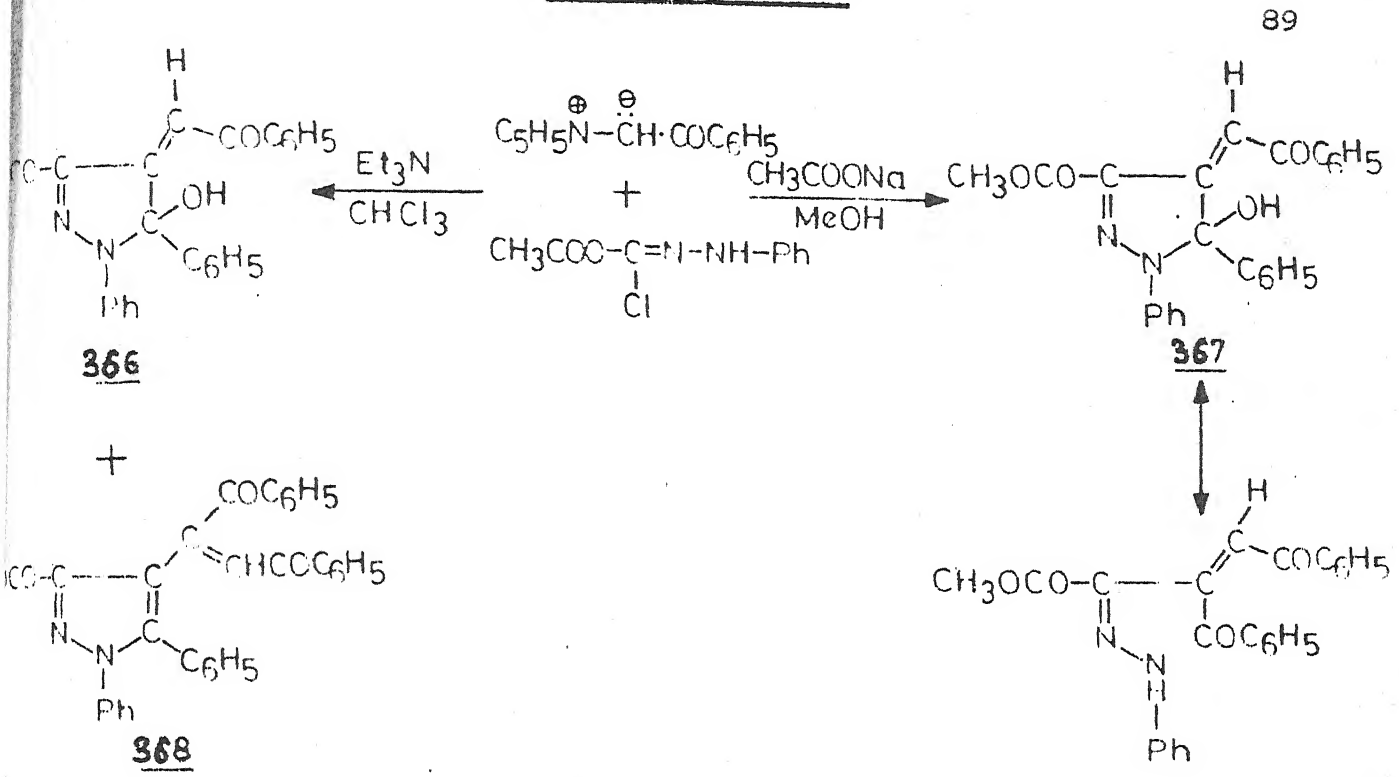
However, the compound (373b) was the exclusive product of the reation of the nitromethane and the isoquinolinium ylid (369b), when triethylamine was used as dehydrohalogenating agent (Scheme I.125).

It is interesting to note that neither N-acetonyl nor N-phenacylidinepyridinium ylids, theirselves, are capable of undergoing similar cyclization reation with nitromethane as isoquinolinium ylids, but the substitution of cyano group at position 3 in the pyridine ring makes the azomethine intermediates as reactive as isoquinolinium ylids[269]. Thus the azomethine intermediates (375) reacted, however with nitromethane resulting in the formation of indolizine derivative (376) following the same reaction sequence (Scheme I.126).

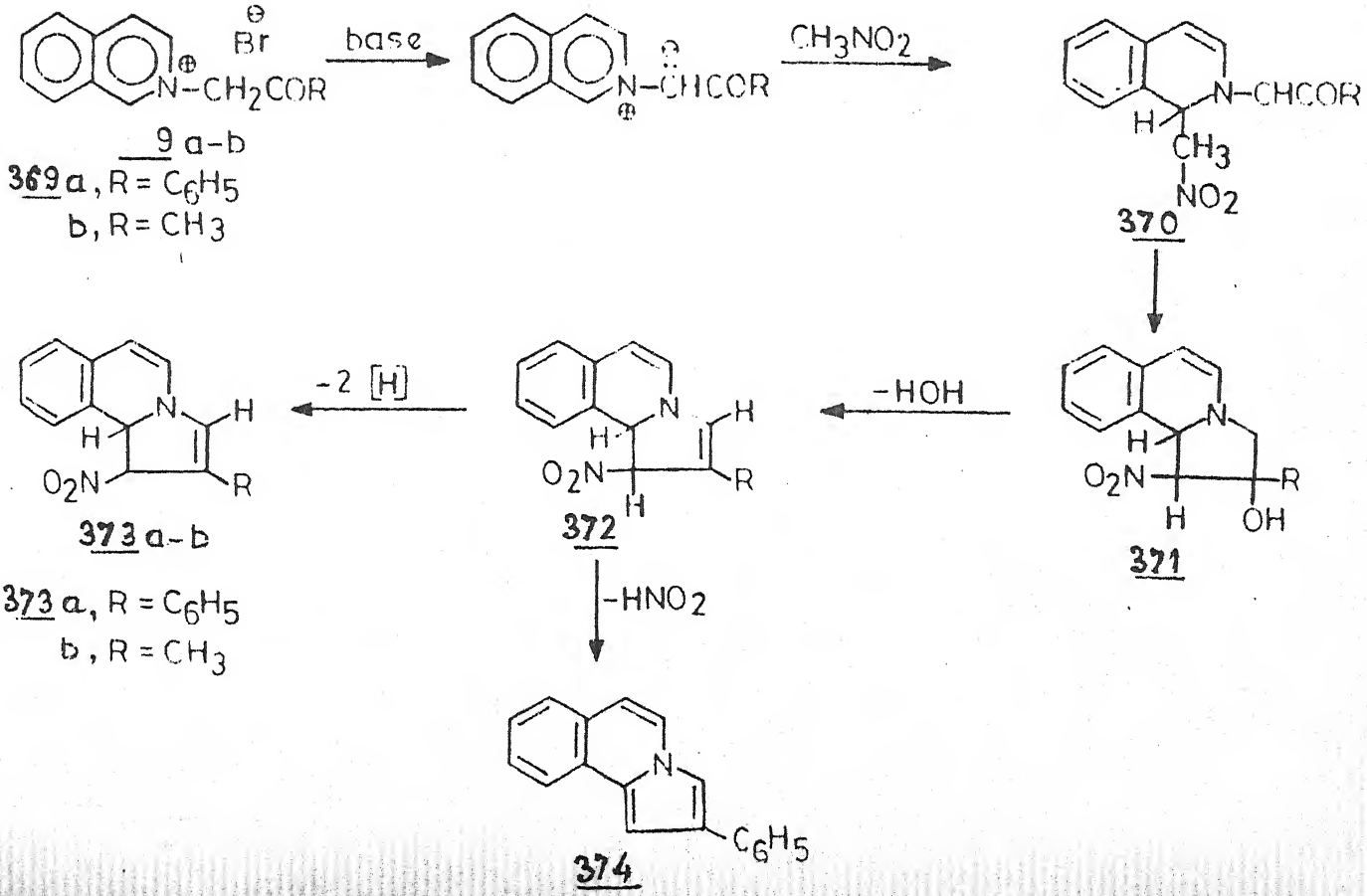
C.2.14. Reaction with diazonium salt[271]

Substituted aroylmethylene azomethine intermediates (361) are capable of undergoing reaction 'in situ' with diazonium salts

Scheme 1.124



Scheme 1.125



particularly obtained from aromatic acids to afford 1,4-dihydro-1,2,4,5-tetrazine (377) in the presence of sodium acetate. (Scheme I.127).

C.2.15 Reaction with amino compounds

(a) Reaction with aliphatic amines and hydrazines

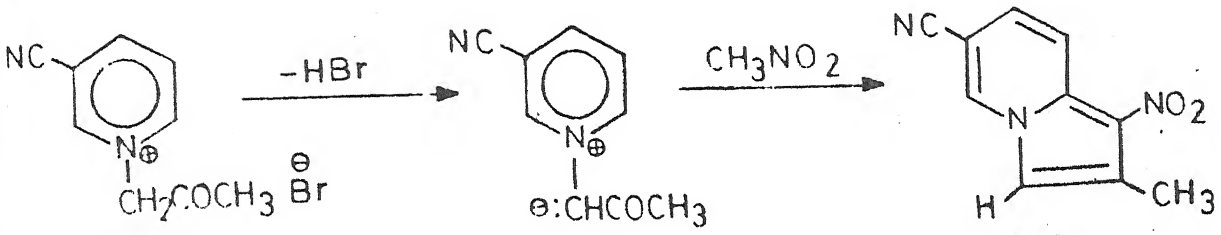
Azomethine intermediates having electronegative substituents in the pyridine ring are only capable of undergoing reaction with aliphatic amines and hydrazines.[257,272]. Thus, 2-bromopyridiniumphenacylids (378 a) with aliphatic amines forms respective imidopyridinium salt (379). On the other hand, 3-cyano substituted azomethine intermediates (378 b) due to strong positive charge in α-position, undergo cyclization reaction to afford cyclopyridinotriamine (380) on treatment with hydrazine hydrate (Scheme I.128).

(b) Reaction with aromatic amines and o-phenylenediamine

Phenacylidene azomethine intermediates and their isoquinolinium counterparts 'in situ', reacts with aromatic amines to afford substituted indol derivatives (381)[257,273,274] in presence of N,N-dimethylaniline under reflux temperature. However, with o-phenylenediamine in boiling acetic acid, these afford 2-phenylbenziamidazole derivatives (382)[275] (Scheme I.129).

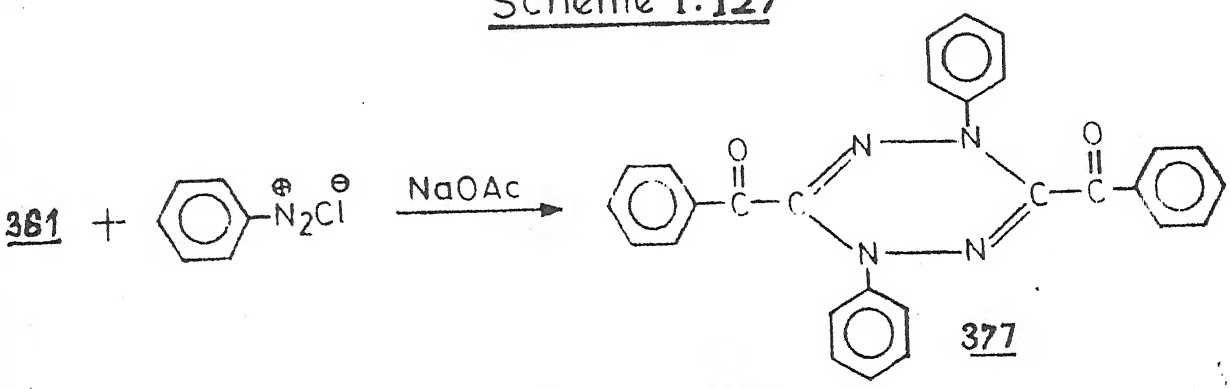
On the other hand, phenacylidene quinolinium ylids (383)

Scheme I.126

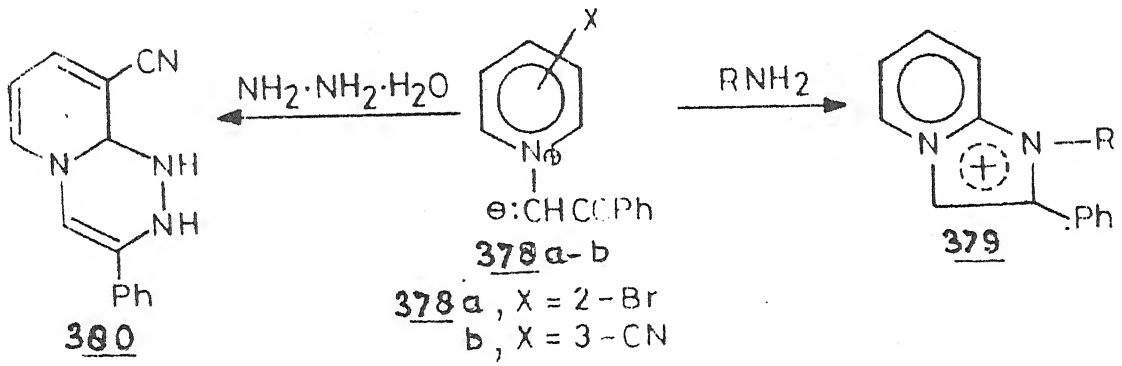


375 376

Scheme I.127



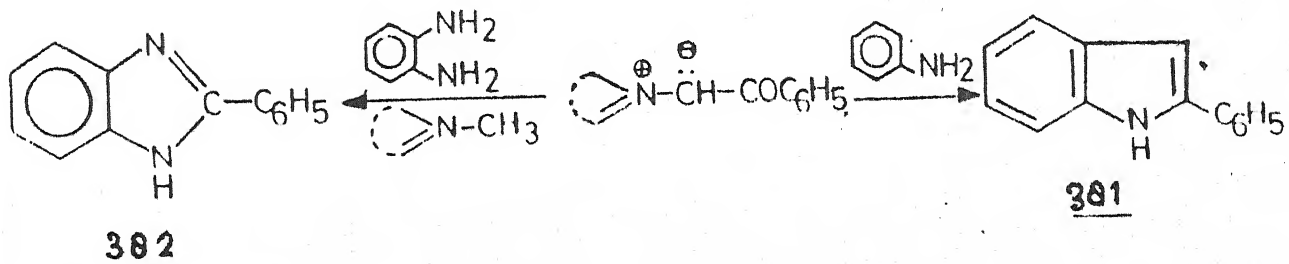
Scheme I.128



380 378 a-b 379

378 a, X = 2-Br
b, X = 3-CN

Scheme I.129



382 381

on their reaction with aromatic amines and o-phenylenediamine follow a different course of reaction due to strong positive character at ∝-position and thus give rise to the formation of dihydroimidazo (1,2a) quinolinium system (384a,b)[257] (Scheme I.130)

However, isoquinolinium ylid generated 'in situ' from their respective salts, follow a different course of reaction with hydrazines and aromatic amines to form triazinophenanthridine derivatives [276] (Scheme I.131).

C.2.16. Cycloaddition reaction of azomethine intermediates

Azomethine intermediates underwent various types of dipolar cycloaddition reactions in presence of dienophiles affording new heterocyclic structures, which are difficult to prepare by using the usual organic synthethic methods.

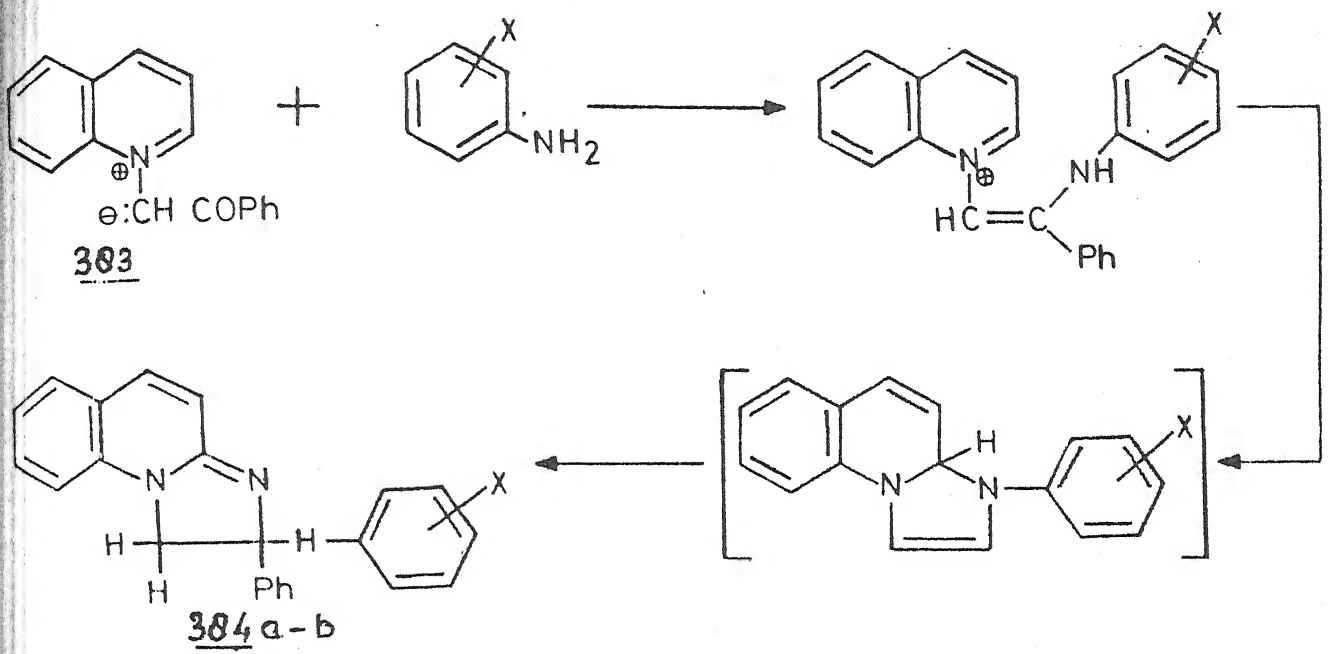
(i) (3+2) Dipolar cycloaddition reactions

(a) Reactions of monosubstituted azomethine intermediates with acetylenic derivatives

Monosubstituted pyridinium methylids undergo cycloaddition with acetylenic philodienes giving indolizines (388). The primary reaction products (387) easily aromatize either by hydrogen transfer to the philodine [277-279] by dismulation [280] (Scheme I.132).

The isoquinolinium methylides react almost similarly with acetylenic dipolarophiles and lead to benzoindolizines (393).

Scheme I.130

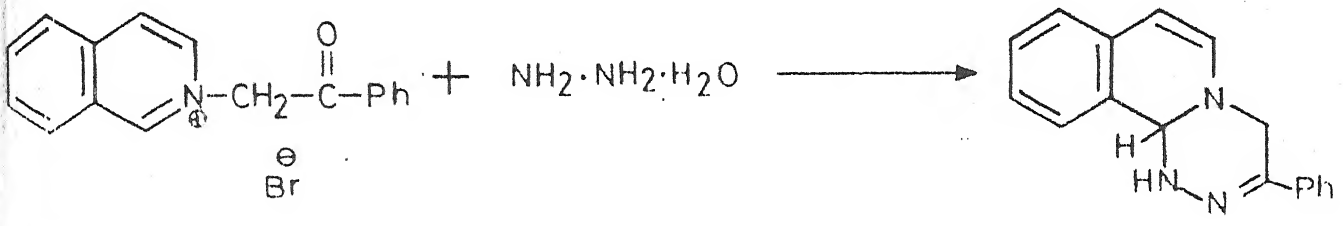


383

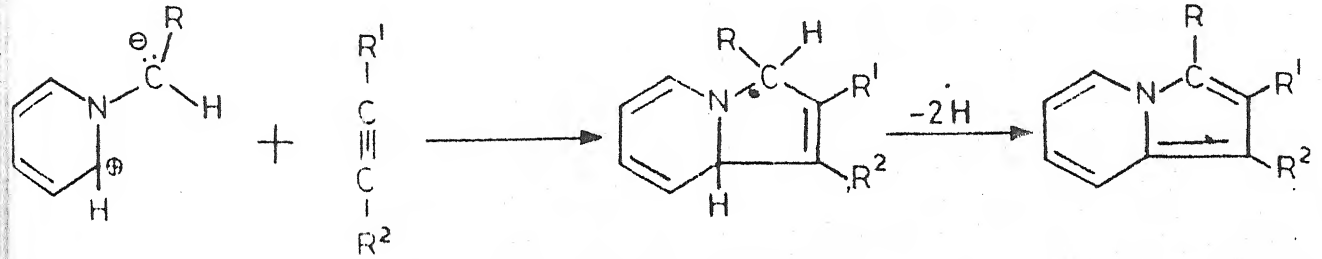
384 a-b

384a, X = H
b, X = 2-NH_2

Scheme I.131



Scheme I.132



385 386 387 388

formed by aromatization of the intermediate dihydroindolizens (390-392)(Scheme I.133). The monosubstituted quinolium ylids behave in exactely similar manner to that of pyridinium methylides.

(b) Reaction of disubstituted azomethine intermediates with acetylenic derivatives

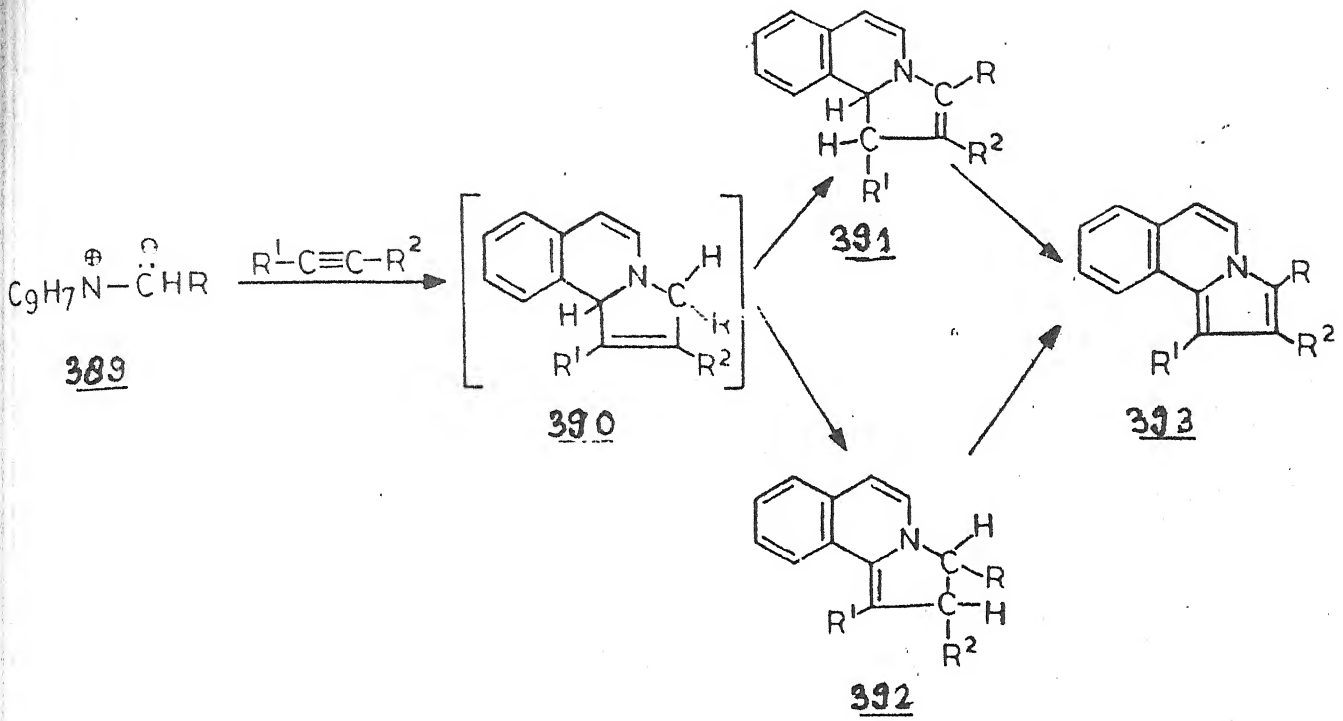
The disubstituted azomethine intermediates give (3+2) type of cycloaddition reactions because of the remaining negative charge on the ylid carbon[201] according to the theoretical calculations, while it was earlier reported that in disubstituted azomethine intermediates, the negative charge of the ylid carbon atom is delocalized on the substituents. It was repoted [202] earlier that the negative charge of the ylid carbon atom, in disubstituted azomethine intermediate is delocalized on the substituents.But according to the theoretical calculations, some negative charge remains on the atom [200]. This explains which ylidic compounds give (3+2) type of cycloadditions.

The pyridinium methylids (394) react with DMAD and leads to the formation of indolizines (396) by the loss of a hydrogen and an ylid substituent (Scheme I.134). Isoquinolinum methylids (397) also react [203,204] with acetylenic derivatives giving indolizine derivatives. Dihydroindolizines (399) and (400) are the usely isolated reaction intermediates (Scheme I.135). The quinolinium ylids, generated 'in situ', on reaction with DMAD in presence of sodium hydride, gives (3+2) cycloadduct (403)[205] (Scheme I.136).

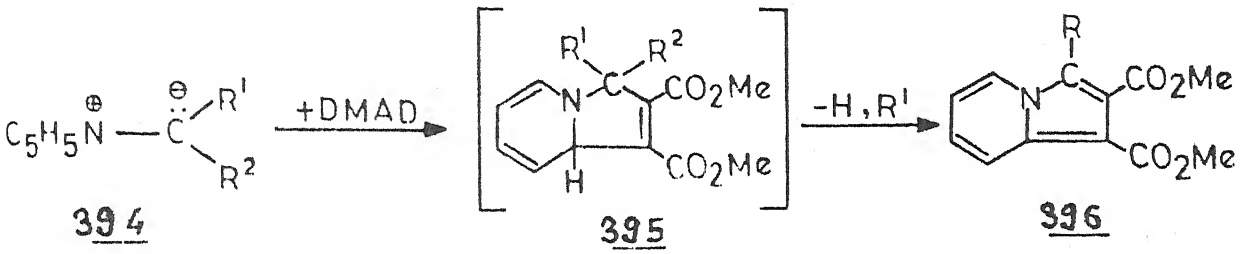
(c) Reaction with ethylenic compounds

Mono- and dicarbethoxyisoquinolinium methylids react

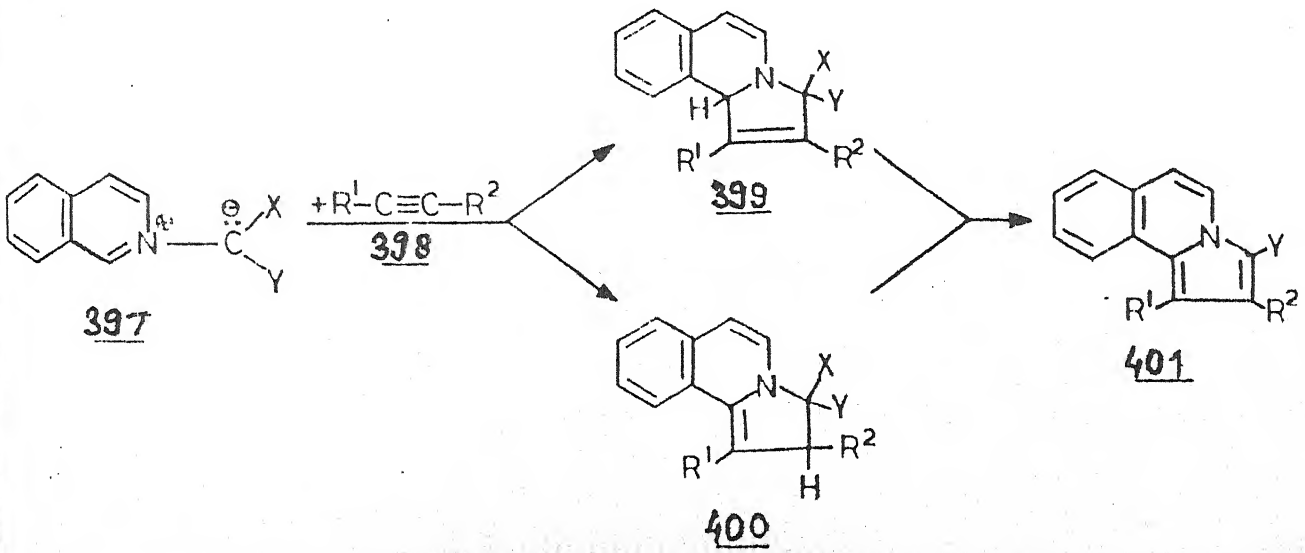
Scheme I.133



Scheme I.134



Scheme I.135



with olefins in presence of methenol and lead to the formation of tetrahydroindolizines (407)[286] with the elimination of an alkyl carbonate molecule from the intermediate (405) (Scheme I.137).

(ii) (5+2) Dipolar cycloaddition reactions

The charge distribution of highly electron withdrawing disubstituted azomethine intermediate is such that they give a 1,5-dipole system (408). Zugravescu et al. [287,288] have isolated oxazepinic derivatives (409) during the reaction of dicarbethoxyisoquinolinium methylids with DMAD in benzene (Scheme I.138).

(iii) (2+2) Dipolar cycloaddition reactions

Cyanocarbethoxy or carbomethoxy azomethine intermediates (410) react with DMAD in presence of acetonitrile and give an ylid (411)[100] (Scheme I.139).

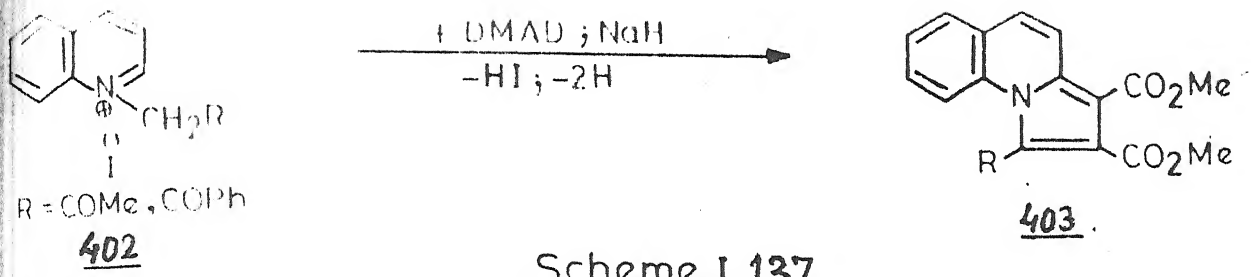
(iv) Cycloaddition involving intermediate formation of an aziridine

The dicarbomethoxyisoquinolinium methylid (412), on reaction with dicyanoacetylene or DMAD, the product (413) is formed in very low yields. The formation of 415 a,b from the aziridine intermediate (414) is the main part of the reaction (Scheme I.140).

C.2.17. Metallation reactions of azomethine intermediates

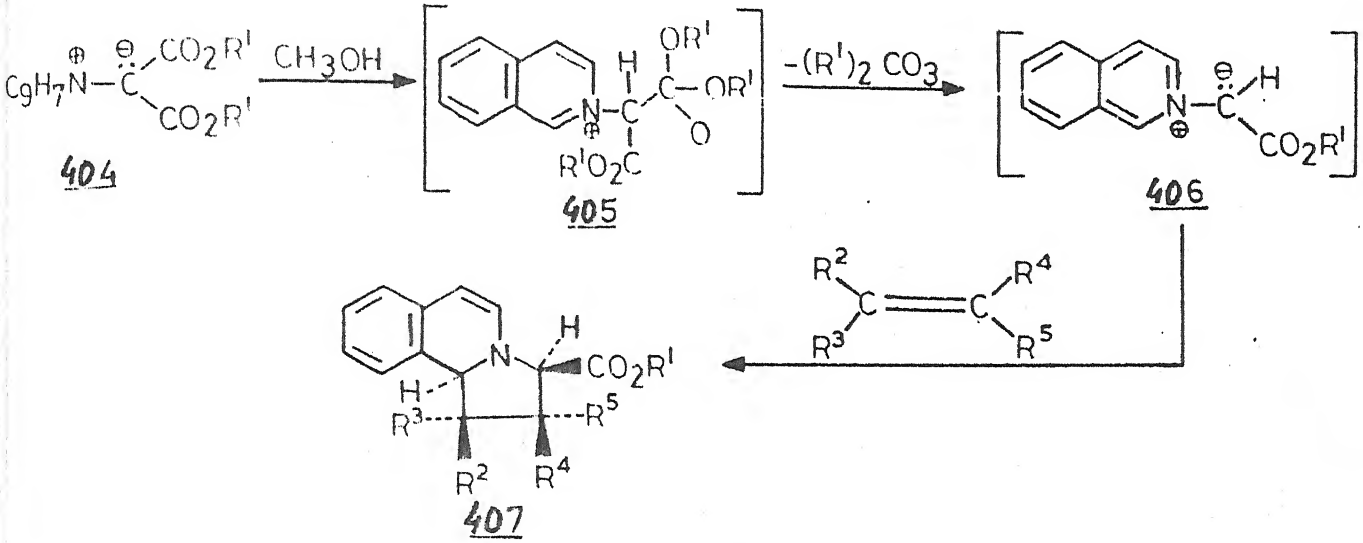
Azomethine intermediates being versatile ligands for

Scheme I.136



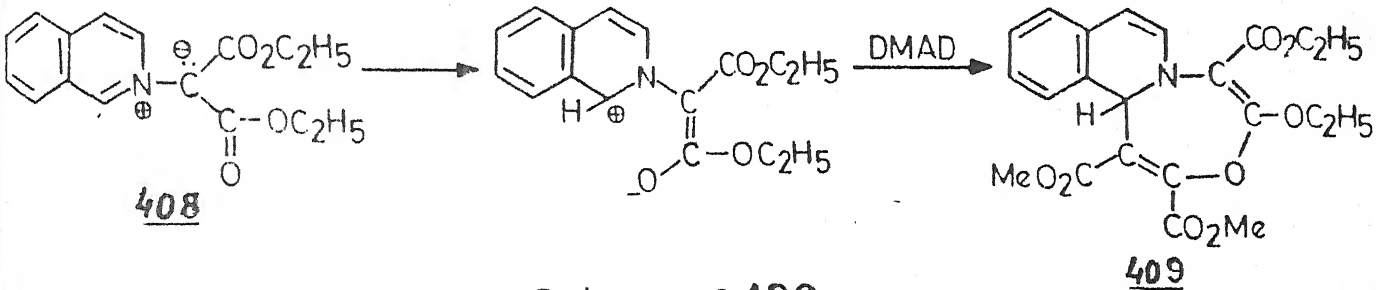
402 403

Scheme I.137



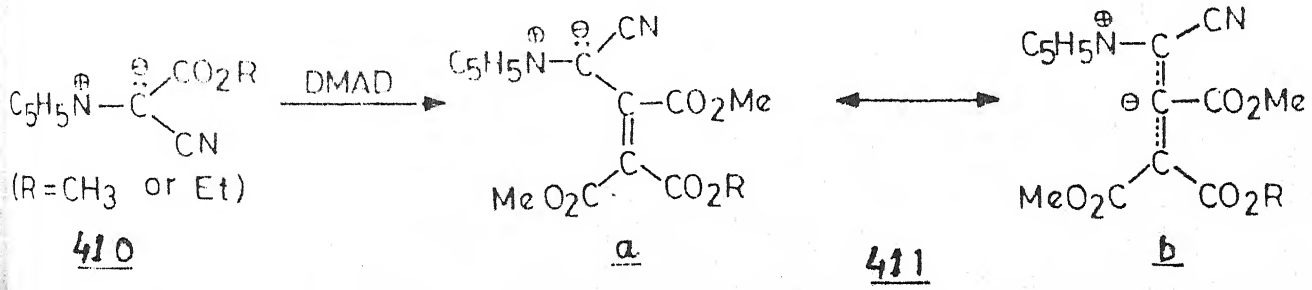
404 405 406 407

Scheme I.138



408 409

Scheme I.139



410 a 411 b

metals, in their various oxydation states,coordinate with metal ions as neutral ligand to form a σ-bond between the ylid carbon and metal atom, hence give rise to ylid- metal complexes[101].

However the mode of reaction and formation of complexes depend upon the reaction conditions, the solvent and the reagent. Pyridiniumphenacylid, on reaction with various metal halides affordsylid- metal complexes (Scheme I.141).

C.2.18. Some spectral properties of azomethine intermediates

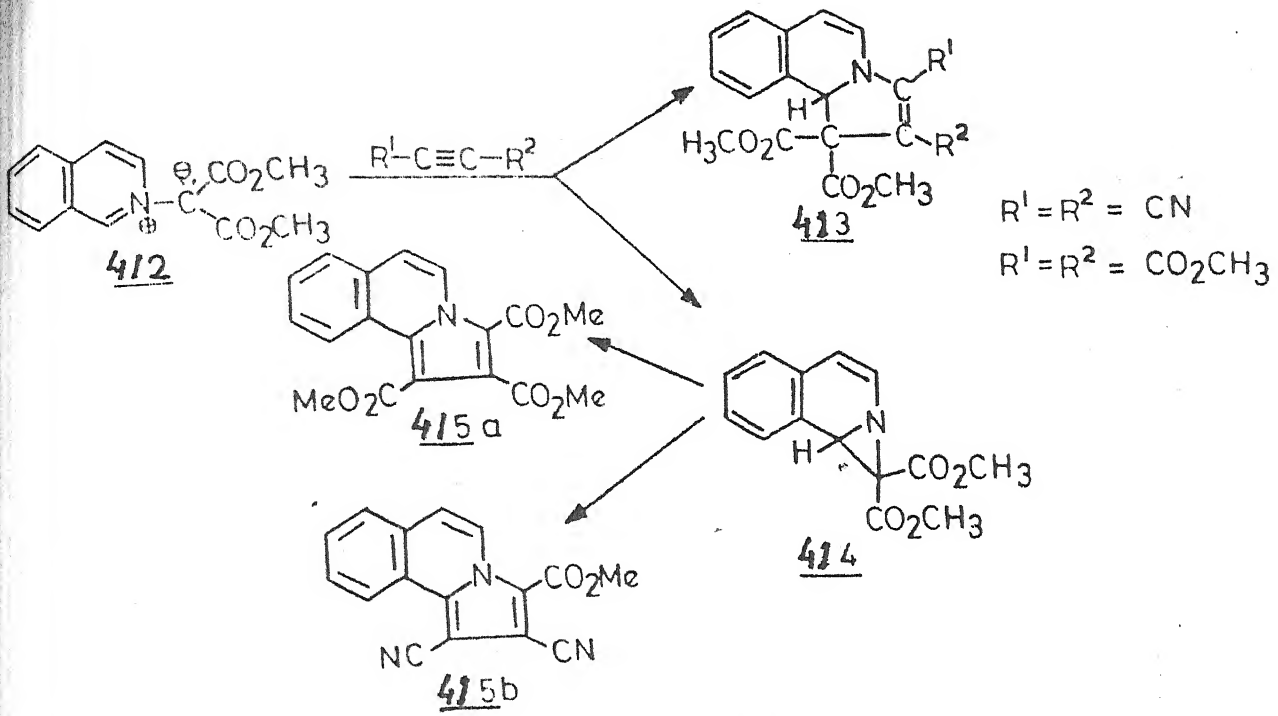
Krohnke and Bohlmann classified as C-betaines, the ylids having maxima at 440-460 mμ as O-betaines,those with maxima 300-330 mu .They concluded that the O-betaines included pyridinium dibenzoylmethylid and C-betaines included all phenacylids. The spectra of pyridinium cyclopentadienylid in several solvents have been studied[102].

Simillarly the visible absorption band of azomethine intermediate is attributed to an intramolecular charge-transfer transition (Scheme I.142).

(a) IR spectra

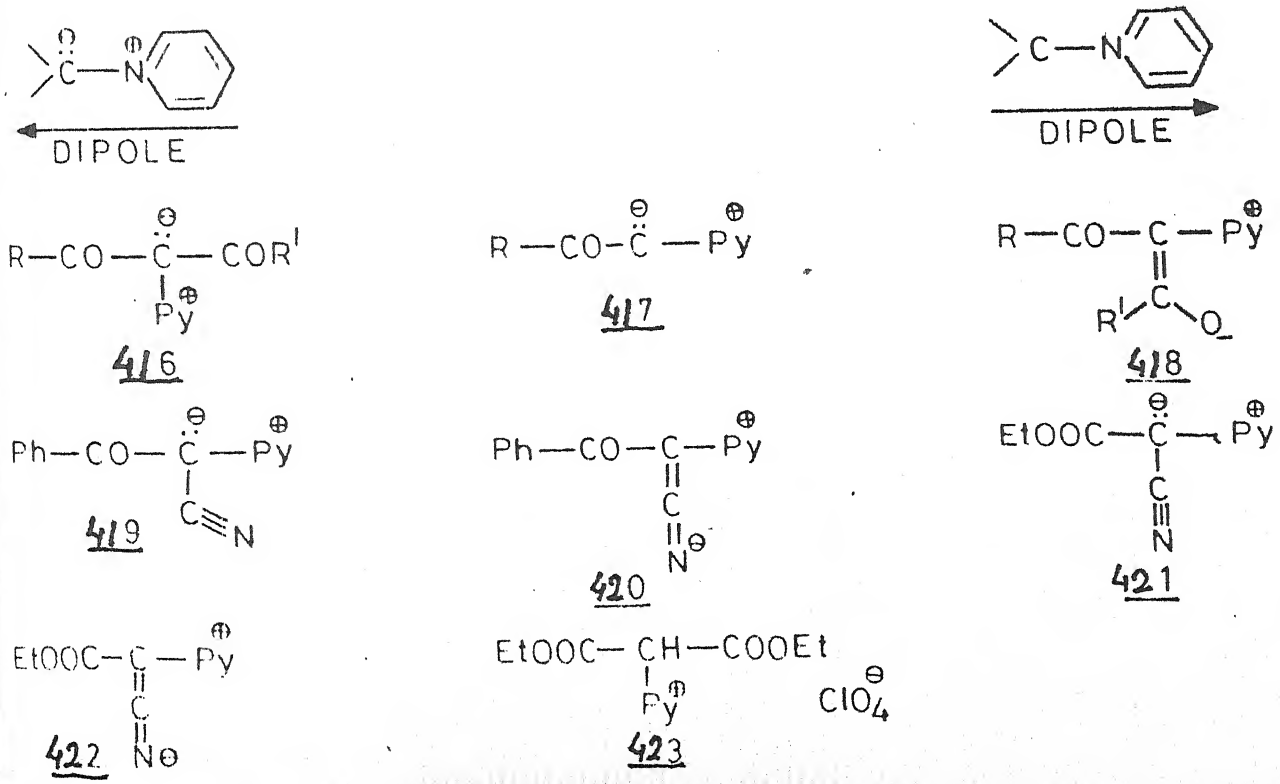
IR spectra of the ylids have been measured in chloroform solution. The spectra are complex but also show strong ylid carbonyl absorption[103-105] at low frequency . Thus the ylid (416) (R = R¹=Ph) absorbs near 1490 cm^{-1} and the ylid (417)(R =Ph) near 1500 cm^{-1}. This presumably indicates, the structure (418) contributes importantly to the resonance hybrids.

Scheme 1.140



Scheme 1.141

Scheme 1.142



The ylid (419) and (421) absorbed strongly at 2166 cm^{-1} and 2185 cm^{-1} respectively, which may also be interpreted as evidence that the stuctures (420 and 422),respectively contribute to the resonance hybrids.

(b) NMR spectra

The most interesting feature of the NMR spectra of the azomethine intermediates is the variation in the chemical shift of the α-proton of the pyridinium ring . In the perchlorate salt of 423, these protons absorbed δ9.21 (d_4-dimetylsulfoxide), but at δ8.63 (deuterochloroform) in the corresponding ylids:

$$EtOOC - \underset{\underset{Py^+ \; ClO_4^-}{|}}{CH} - COOEt$$

Simillarly values were observed for α-protons in the ylid (416) (R = Me,R^1=Ph) and (418) (R = R^1=Ph) . This shift is to be expected because of the overall increase in electron density. However, in the cyano ylids (419 and 421), the α-proton absorbed well downfield at δ 9.23 and δ 9.31 respectively (deuterochloroform),but the β - and γ-protons are not deshielded. This effct may also be explicable in terms of contributions of the structures 420 and 422.

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CHAPTER II

REACTIONS OF PHOSPHORANE INTERMEDIATES (PHOSPHONIUM YLIDS) WITH HETEROCYCLIC KETONES AND THIOKETONES: SYNTHESIS OF SOME NEW SUBSTITUTED-1,2-DITHIAFULVENES.*

II.1 ABSTRACT

A wide variety of 5- phenyl-4-aryl-1,2-dithiafulvenes and 5-phenyl- 4-aroyl-1.2-dithiafulvenes have been synthesized by the interaction of 5- phenyl -1,2- dithiole-3-one and phosphorane intermediates. The synthesis of these dithiafulvenes have also been carried out by an alternativ route which involves the condensation of phosphorane intermediates with 5-phenyl -1,2-dithiole- 3- thione. The spectral data for the resulting products were consistent with the preposed structure of the products.

II.2 INTRODUCTION

Many routes have been devised to enable the introduction of exocyclic double bonds at C-3 position of 1,2-dithiole ring to form substituted -1,2- dithiafulvenes. Thus Leaver [1] has prepared 5,4- diphenyl-1,2- dithiafulvenes(2) by deprotonation of 5- phenyl-3- benzyl-1,2- dithiolium salt (1) with aqueous soda solution (Scheme II.1). However, the same

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worker and others [2] have developed an alternative route for the preparation of 5- aryl - 6-benzoyl-1,2- dithiafulvenes (5) which involves the interaction of sodium salt of active methylene compound (4) with trithiolium salt (3) (Scheme II.2).

Lazach et al.[3] and Traverso [4,5] have also achieved the synthesis of 1,2- dithiafulvenes (8) by reacting potassium hydrogen sulfide with pyran- 4- thione (6) and thiapyran- 4- thione (7) (Scheme II.3). This method was proved to be superior to aforementioned method because it involved mild reaction conditions and afforded desired products in appreciable yields. Later on, Pfister et al.[6,7] developed another method for the synthesis of 1,2- dithiafulvenes (10) which involves the interaction of sulfur upon ∝- (Cinnamylidene) Ketone (9) (Scheme II.4). But this method was found to be less versatile, owing to the side reactions which resulted in formtion of thiophene derivative along with desired product (10). It is matter of chance that the ylid intermediates, which have of late been used in the creation of exocyclic double bonds, have not been utilized in the synthesis of 1,2- dithiafulvenes. Prompted from this, it seemed to be of interest to explore a new route to bring about the conversion of carbonyl function at C-3 of thiole ring into exocyclic double bond.

In the present chapter, we have, therefore developed a convenient and facile route for the synthesizing substituted 1,2 — dithiafulvenes via the interaction of phosphorane intermediate with 5- phenyl-1,2 — dithiole-3-one and

5-phenyl-1,2- dithiole-3-thione.

II.3RESULTS AND DISCUSSION.

Quaternization of triphenylphosphine with substituted benzyl bromides, 2-bromomethylnaphthalene, 1-bromo-2-bromomethylnaphthalene and substituted phenacyl bromides at reflux temperature gave phosphonium salts, substituted benzyltriphenylposphonium bomides (11a-h), naphthylmethyltri phenylphosphonium bromides (11i-k) and phenacyltriphenyl phosphonium bromides (11 l-o) in good yields. Treatment of these phosphonium salts (11a-o) with sodamide or sodium hydride in benzene effected proton abstraction yielding corresponding ylids, substituted benzylidenetriphenylphosphoranes (12a-h), 2-naphthylmethylenetriphenylphosphoranes (12j-k) and phenacylidene-triphenylphosphoranes (12l-o) (Scheme II.5). The reaction of semi - stabilized phosphorane intermediates (12a-k) with 5-phenyl - 1,2- dithiole - 3 - one (13a) and 5 - phenyl - 1,2-dithiole - 3 - thione (13b) were carried out at room temperature to give 5 - phenyl - 6 - substituted aryl - 1,2 - dithiafulvenes (5- phenyl - 3 - arylidene - 1,3 - arylidene - 1,2 - dithioles) (14a-k) in 40 - 80 % yields (Scheme II.5)

However, reaction of carbonyl stabilized ylids, p-substituted phenacylidenetriphenylphosphorane (12l-o), with ketone (13a) or thioketone (13b) gave 5 - phenyl - 6 - substituted benzoyl - 1,2 - dithiafulvenes (5 - phenyl - 3 - substituted phenacylidene - 1,2 - dithioles) (14l-o) in 50 - 80 %

yields (Scheme II.5).

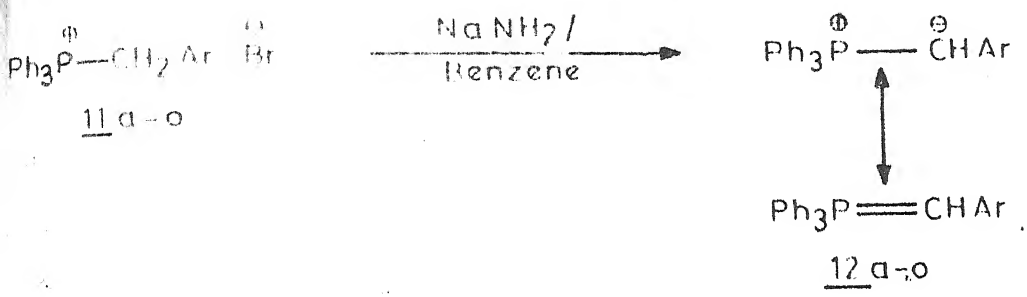
The ketone (13a) was found to be more reactive than the thioketone (13b) since former when condensed with ylides (12a-o) afforded better yields of products (14a-o). It was also interesting to note that the position of substituents in the dithiole ring has great effect in carbonyl olefination. Thus 4-phenyl - 1,2 - dithiole - 3 - thione failed to couple with phosphorane intermediates (12a-o), probabaly due to steric hindrance caused by phenyl ring.

All the 1,2 - dithiafulvenes (14a-o) gave satisfactory elemental analyses. Melting points of the products (14a-o), prepared by the olefination of ketone (13a), are very close to those prepared by the olefination of thioketone (13b). The IR spectra of products (14a-k) showed absorption bands at 1605 - 1585 cm^{-1} (C=C) and 970 - 958 cm^{-1}. The latter absorption bands were associated with out of plane deformations of the hydrogen atom attached to carbon carbon double bond [9]. In case of compounds (141 - o), the carbonyl stretching region was not found in the usual rang [9] 1720 - 1620 cm^{-1}, but strong bands were found in the range 1620 - 1520 cm^{-1}. The NMR spectra, [9] in general, exhibited olefinic protons in the range of δ6.80 - 7.40, olefinic protons of dithiole ring in the range of δ7.00 - 7.45 and aromatic protons at 7.20 - 8.50 (Table II.2).

II.4 EXPERIMENTAL

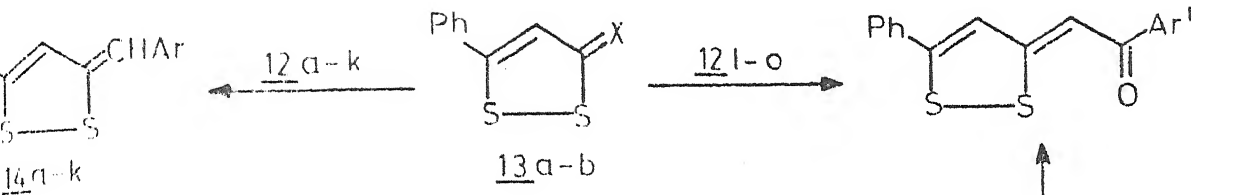
II.4.1 General techniques

Scheme II.5



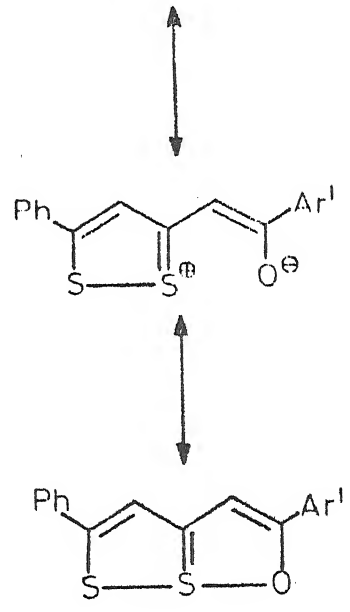
11 a-o

12 a-o



14 a-k

13 a-b

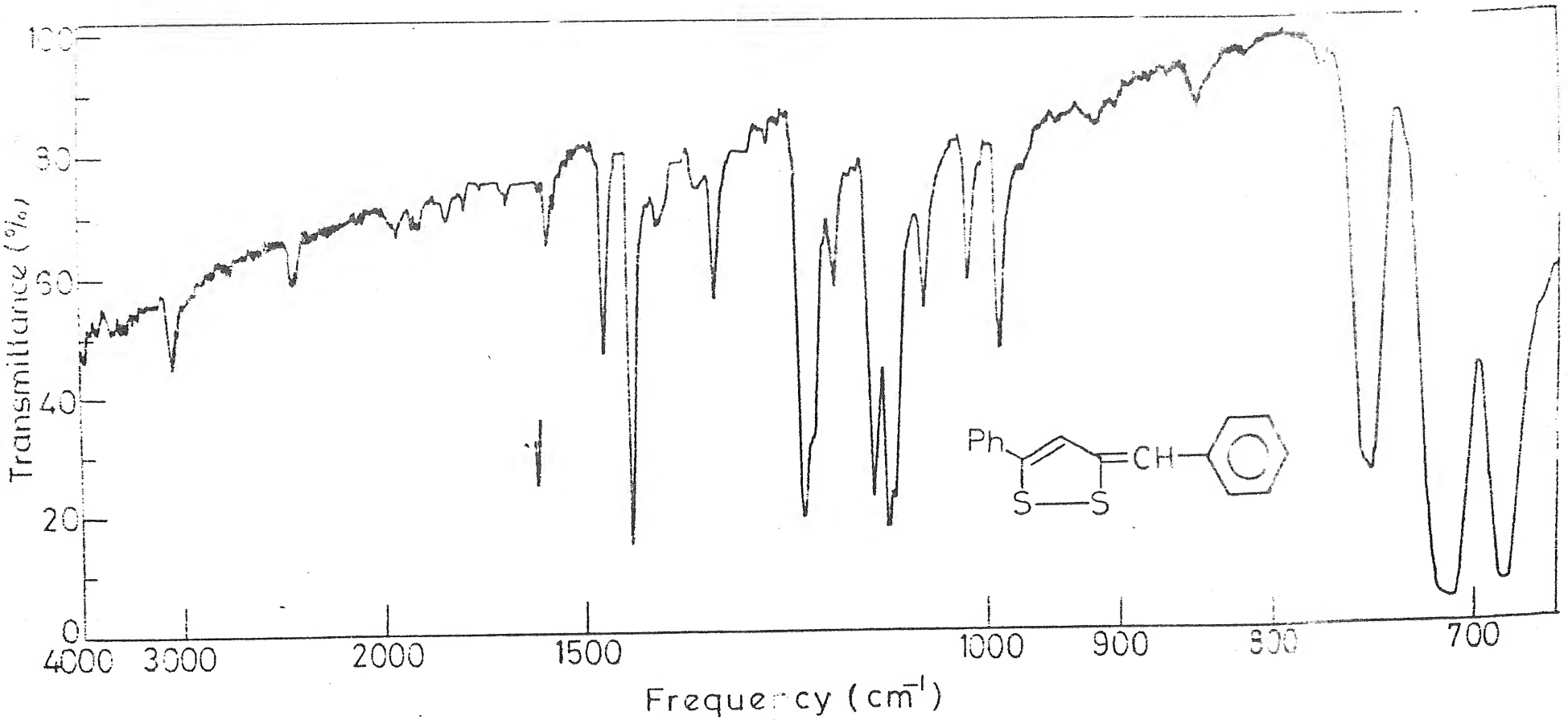


14l-o

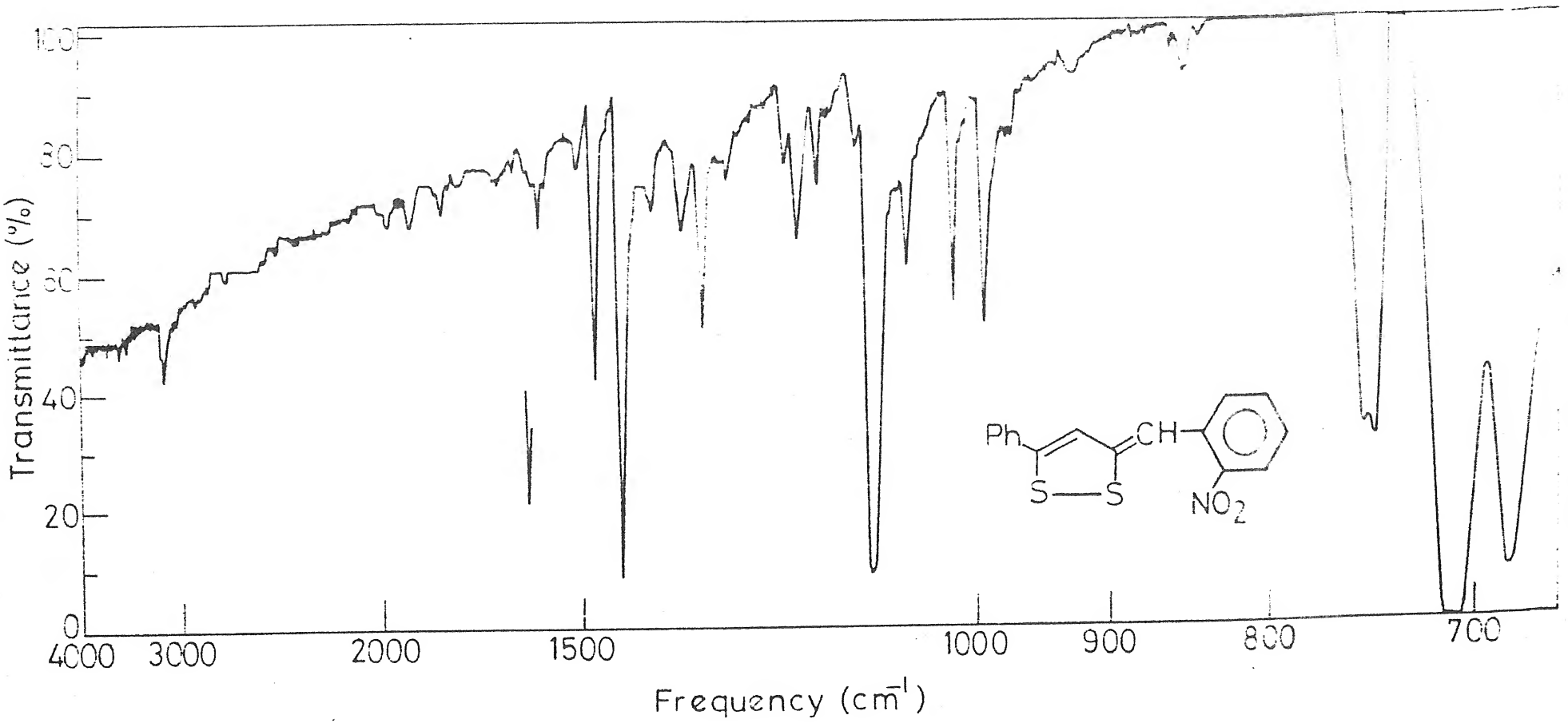
12 and 14a, Ar = C_6H_5
b, Ar = 2-$NO_2C_6H_4$
c, Ar = 3-$NO_2C_6H_4$
d, Ar = 4-$NO_2C_6H_4$
e, Ar = 4-ClC_6H_4
f, Ar = 4-IC_6H_4
g, Ar = 4-$CH_3C_6H_4$
h, Ar = 4-$CH_3OC_6H_4$
i, Ar = 2-$C_{10}H_7$
j, Ar = 1-Br-2-$C_{10}H_6$
k, Ar = PhCH=CH

12l, Ar' = C_6H_5CO
m, Ar' = 4-ClC_6H_4CO
n, Ar' = 4-$CH_3C_6H_4CO$
o, Ar' = 4-$CH_3OC_6H_4CO$

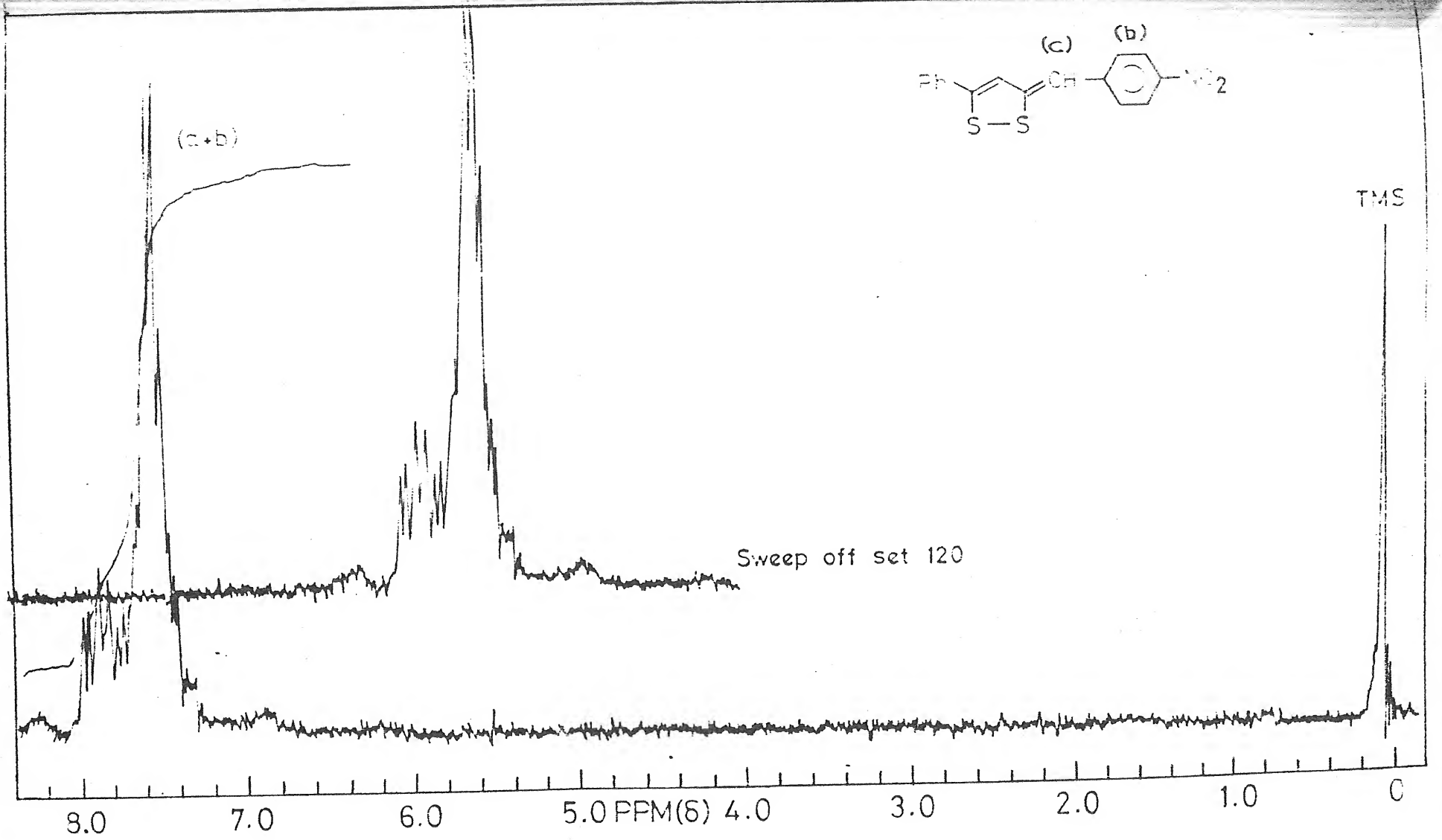
14l, Ar' = C_6H_5
m, Ar' = 4-ClC_6H_4
n, Ar' = 4-$CH_3C_6H_4$
o, Ar' = 4-$CH_3OC_6H_4$



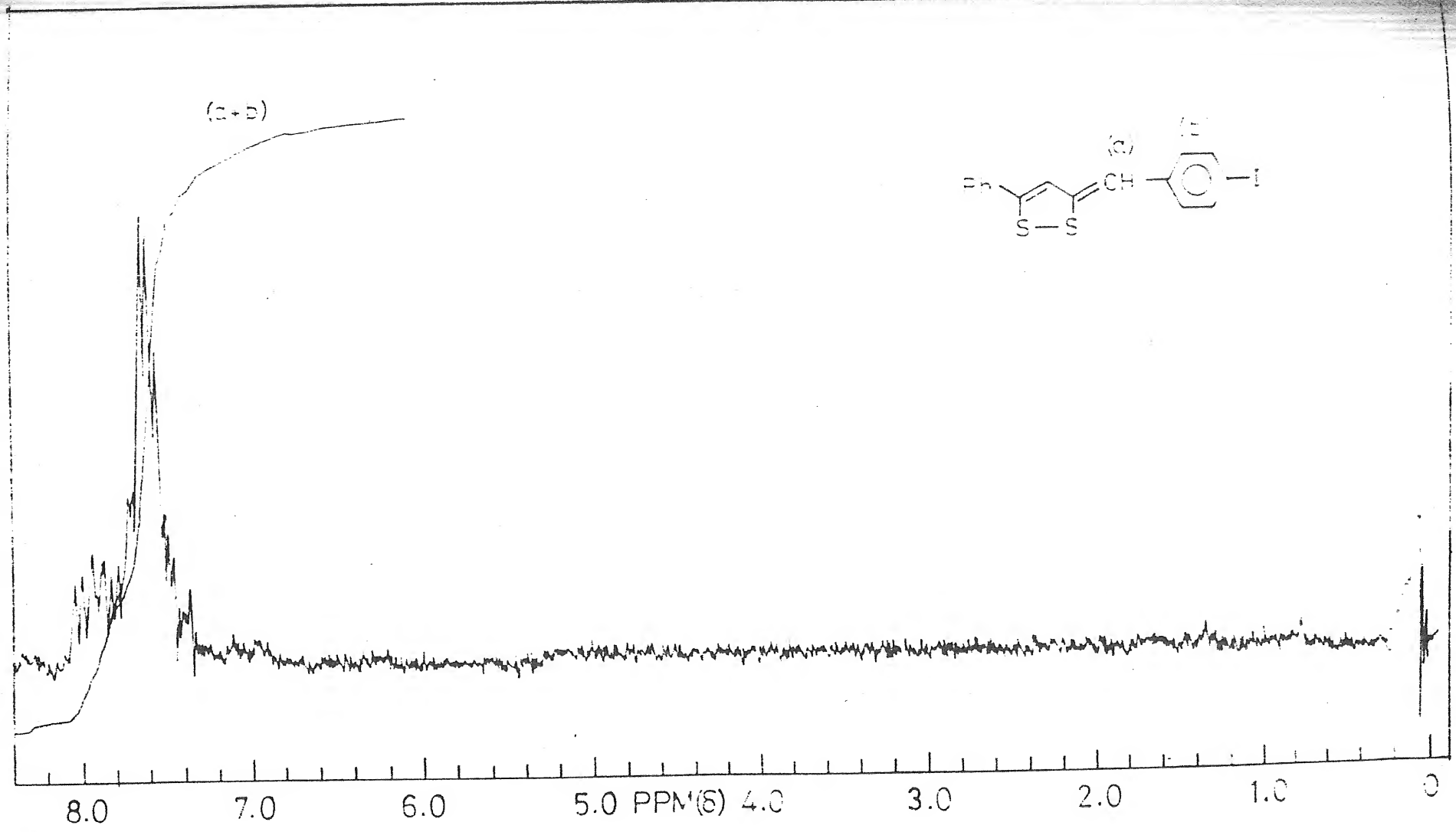
IR spectrum of 5-phenyl-3-benzylidene-1,2-dithiole (14a)



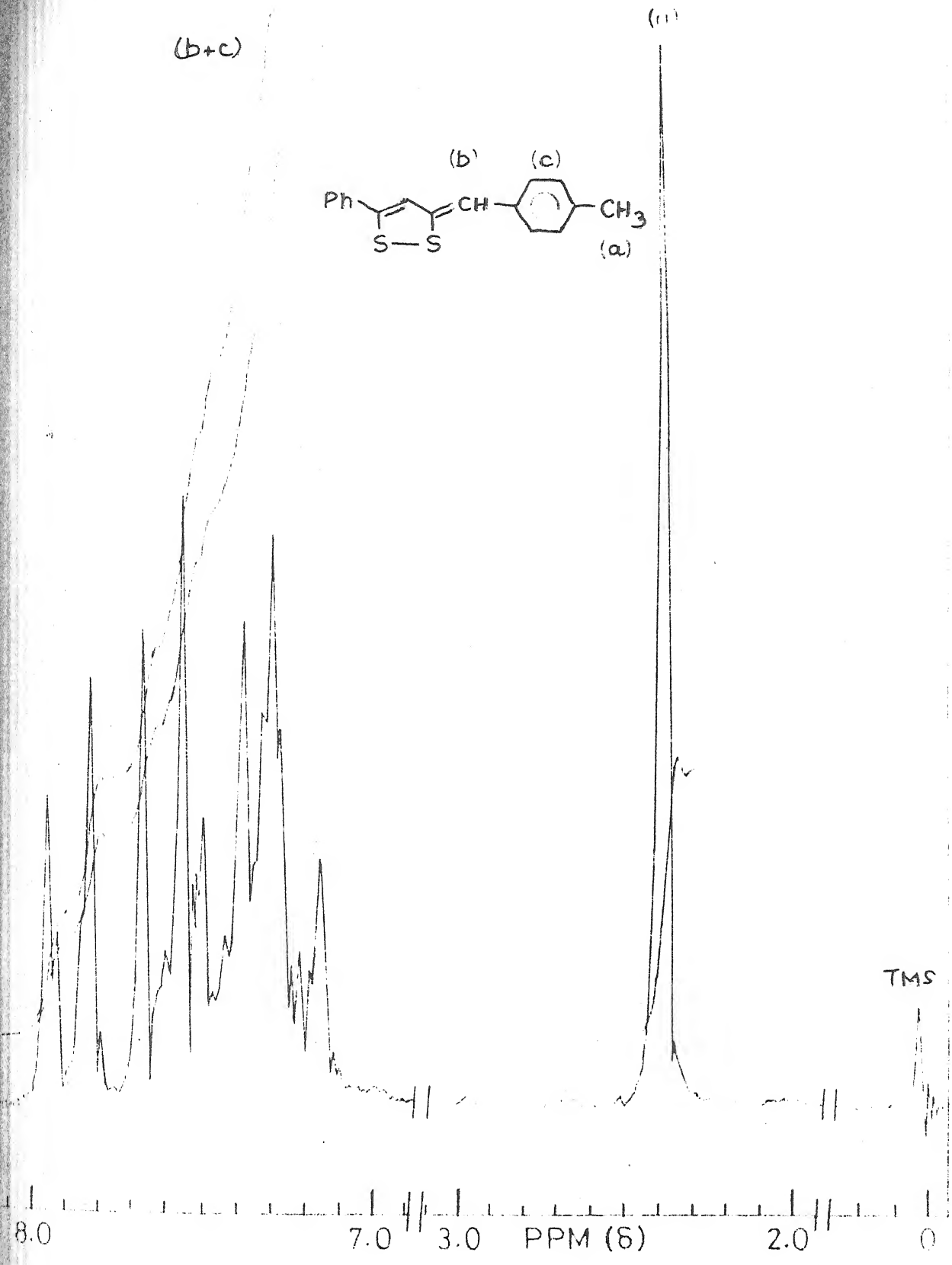
IR spectrum of 5-phenyl-3-(2-nitrobenzylidene)-1,2-dithiole (14 b).



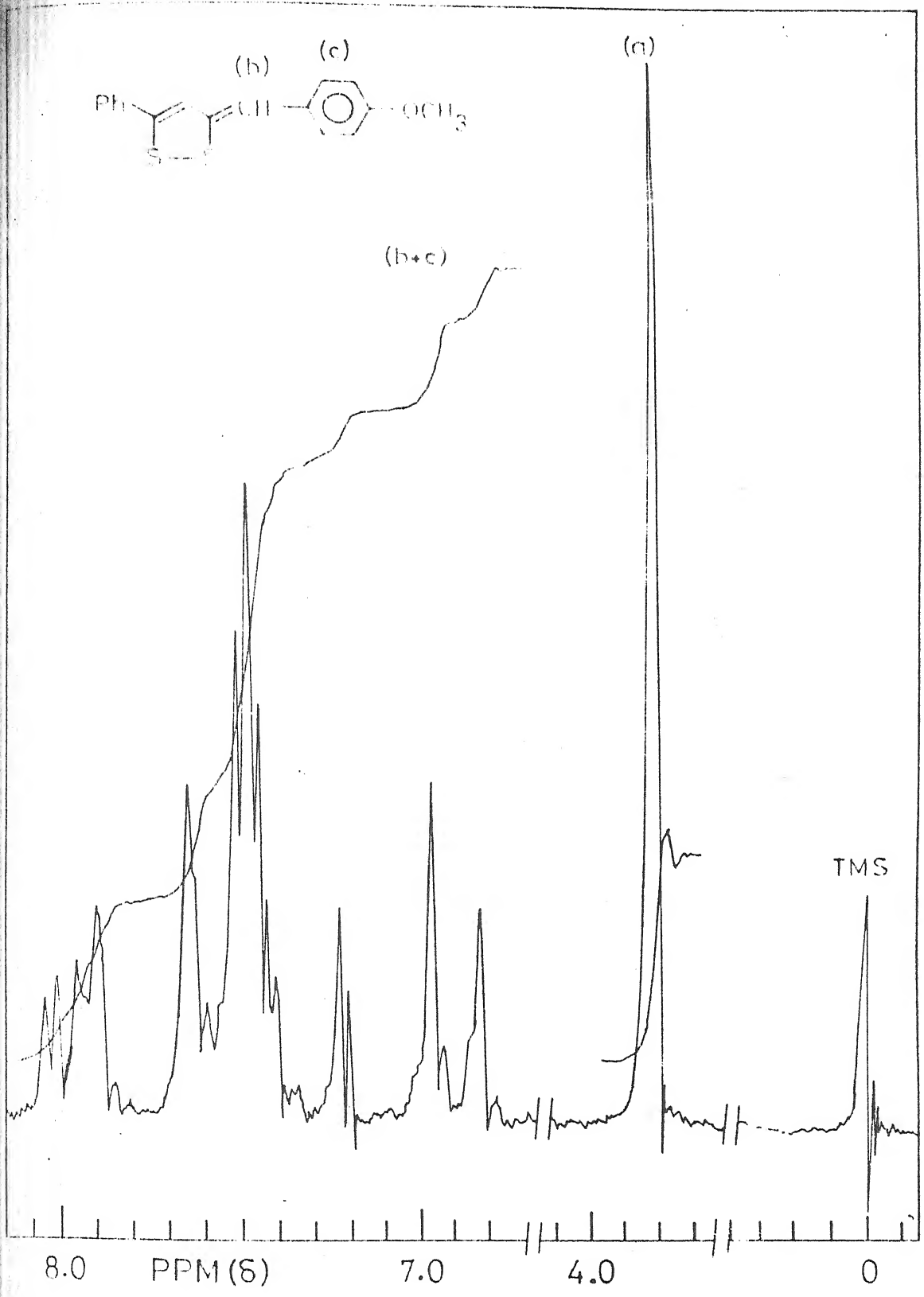
NMR spectrum of 5-phenyl-3-(4-nitrobenzylidene)-1,2-dithiole (14d).



NMR spectrum of 5-phenyl-3-(4-iodobenzylidene)-1,2-dithiole (14f



NMR spectrum of 5-phenyl-3-(4-methylbenzylidene)-1,2-dithiole (14g)



NMR spectrum of 5-phenyl-3-(4-methoxybenzylidene)--1,2-dithiole (14h)

Unless otherwise specified here and hereinafter, melting points are uncorrected, reported in degrees centrigrade and determined on a Gallen Kamp apparatus. IR spectra (KBr) were recorded on a Perkin - Elmer infracord spectrophotometer. The NMR spectra were recorded ($CDCl_3$) on a varian A - 60 spectrometer using TMS as internal standard. All the products were separated and purified by column chromatography using alumina ; purity was checked by TLC for which glass microscope slides coated with silica gel G were used . and the spots on these slides were detected by iodine.

II.4.2 Starting materials

All the reagents were obtained from comercial sources (BDH, E.Merck). The ketone (13a) and thioketone (13b) were prepared according to the method reported in the literature[10]. All the phosphonium salts (11a-O) were prepared by heating triphenylphosphine with substituted alkyl halides in anhydrous benzene at reflux temperature.

II.4.3 Preparation of substituted phosphonium salts

II.4.3.1 Preparation of substituted benzyltrithenylphosphonium salts (11a -h)

A mixture of 0.43 mole of substituted benzyl bromide and 0.5 mole of triphenylphosphine in 50 ml of benzne was refulxed and stirred for 8 - 10 hrs. After cooling, the salt was filtered, washed with ether and dried under reduced pressure . The product

was crystallized from chloroform and benzene to give clusters and coulerless crystals of desired products. Thus, from aforesaid method following salts are prepared –

(i) Benezyltriphenylphosphnium bromide (11a) : m.p.– 250 – 52°C (lit.m.p. – 252 – 53°C)[12]

(ii) O– nitrobenzyltriphenylphosphonium bromide (11b) : m.p.– 288 – 89°C (Lit.m.p.– 285 – 87°C) [11].

(iii) m– nitrobenzyltriphenylphosphonium bromide (11c) : m.p. – 290 – 92°C (Lit.m.p. – 288 – 90°C) [12]

(iv) p– nitrobezyltripheneylphosphonium bromide (11d) : m.p.– 275 – 77°C (Lit.m.p. – 280°C) [12]

(v) p – chlorobenzyltriphenylphosphonium bromide (11e) :m.p. – 278 – 80°C (Lit.m.p. – 276 – 77°C) [13]

(vi) p–iodobenzyltriphenylphosphonium bromide (11f): m.p. – 256 – 57°C (Lit.m.p. –254 – 55°C)[14]

(vii) p– methylbenzyltriphenylphosphonium bromide (11g) : m.p. –276 – 77°C (Lit.m.p. –280 –81°C) [12].

(viii) p–methoxybenzyltriphenylphosphonium bromide (11h) : m.p. – 245 – 46°C(Lit.m.p. –247– 48°C) [13].

II.4.3.2 Preparation of substituted naphthylmethyltriphenyl phosphonium salts (11i–k)

0.25 mole of substituted bromomethylnaphthalene and 0.30 mole of triphenylphosphine in 100 ml of benzene was heated for 5–7 hrs with stirring. After heating upto boiling the mixture was cooled to room tempareture and left for 2–3 hrs without

disturbing leading to the precipitation of the desired product which was filtered off. It was washed with ether and dried under reduced pressure. The sample was crystallized from cholpform and petroleum ether. Thus the white crystals of the salts were fromed. From this method following salts are prepared.

(i) 2- naphthylmethyltriphenylphosphonium bromide (11i) :m.p. - 245- 47°C (Lit.m.p.- 243 - 45°C) [16].

(ii) 1- bromo - 2- naphthylmethyltriphenylphosphonium bromide (11j) : m.p. - 238 - 40°C (Lit. m.p. - 240°C) [17].

(iii) Cinnamyltriphenylphosphonium bromide (11k) :m.p. - 246 - 48°C (Lit.m.p.- 250C) [12]

II.4.3.3 Preparation of substituted phenacyltriphenylphosphonium salts (11l-O)

Substituted phenacyl bromide (0.4 mole) was added in portions to a chloraform (75 ml) solution of triphenylphosphine (0.4 mole). This solution was refluxed for 8 - 10 hrs. Then the solution was filtered into one litre of anhydrous ether. The precipitate was collected and dried. The salt was recrystallised from methanol - ethyl acetate. Thus following salts was prepared.

(i) Phenacyltripheylphosphonium bromide (11l) :m.p. - 279 - 80°C (Lit.m.p. 281 - 82°C) [18].

(ii) p - chlorophenacyltriphenylphosphonium bromide (11m) : m.p. -250-52°C (Lit. m.p.- 253-54°C) [19]

(iii) p- methylphenacyltriphenylphosphonium bromide (11n) :m.p. - 260-62°C (Lit.m.p.- 262-63°C) [19]

(iv) p- methoxyphenacyltriphenylphosphonium bromide (11o) :m.p. - 244-45°C (Lit. m.p. 243-44°C)[19]

II.4.3.4. Preparation of 5- phenyl - 6 - aryl-1,2 -dithiafulvenes (14a -k).

To a stirred suspension of ylid (12a-l), generated from 4 mmole of its salt (11a-k) and 5 mmole of sodamide in 100 ml of anhybrous benzene, was added dropwise through a dropping funnel a solution of 4 mmole of ketone (13a) or thioketone (13b) in 20 ml of benzene during a period of 30 minutes. The mixture was then stirred at the room temperature for 6 -12 hrs. The residue containing triphenylphosphine oxide and unreacted sodamide was filtered and filtrate was concentrated on a steam bath under reduced pressure. The resulting mass was chromatographed over neutral alumina using petroleum ether (40 - 60°C) - benzene (1:2) as eluant to give desired products (14a-k) which were further recrystallized from appropriate solvents (Table II.1).

II.4.3.5 Preparation of 5- phenyl - 6 - aroyl-1,2-dithiafulvenes (14 l-o)

To a mixture of 4 mmole of salt (11l-o) and 5 mmole of sodamide in 100ml of anhydrous benzene, was added under nitrogen, 4 mmole of ketone (13a) or thioketone (13b). The mixture was refluxed for 8-16 hrs and left over night. The residue was filtered off and filtrate was evaporated on a steam bath. The resulting mass was chromatographed. Elution from petroleum ether

-benzene (1:1) gave desired products (141-o) in 60 -80% yields which were recrystalllized from suitable solvents (Table II.1).

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Table II.1 :Physical Properties of 5-phenyl -3-arylidene -1,2-dithioles (14a-o)

compound	Ar	m.p. (°C)	yield(%) via route A	yield(%) via route B	Recrystn. solvent	Analysis found/ (calculated)% C	H
1	2	3	4	5	6	7	8
14 a	C_6H_5	134-36	80	65	EtOH	71.61	4.43
						(71.64)	(4.47)
b	$2-NO_2C_6H_4$	128-30	70	60	C_6H_6-hexane	61.31	3.48
						(61.34)	(3.51)
c	$3-NO_2C_6H_4$	230-32	65	52	EtOH	61.33	3.50
						(61.34)	(3.51)
d	$4-NO_2C_6H_4$	142-44	84	75	$CHCl_3$	61.32	3.49
					Pet ether	(61.34)	(3.51)
e	$4-ClC_6H_4$	155-58	58	40	EtOH	63.50	3.65
						(63.47)	(3.63)
f	$4-IC_6H_4$	148-50	50	45	EtOH	48.78	2.78
						(48.73)	(2.79)
g	$4-CH_3C_6H_4$	112-14	45	35	$CHCl_3$-C_6H_6	72.31	4.91
						(72.34)	(4.94)
h	$4-CH_3OC_6H_4$	148-50	65	50	EtOH	68.40	4.71
						(68.45)	(4.69)

Table II.1 (Contd.)

1	2	3	4	5	6	7	8
i	2-$C_{10}H_7$	140	70	50	$CHCl_3$/ hexane	75.43 (75.47)	4.42 (4.40)
j	1-Br-2-$C_{10}H_6$	258-60	50	40	EtOH	60.50 (60.45)	3.25 (3.27)
k	C_6H_5CH=CH-	128-30	60	50	EtOH	73.48 (73.47)	4.72 (4.76)
l	C_6H_5CO-	130-32	60	50	EtOH	71.36 (71.33)	4.10 (4.13)
m	4-ClC_6H_4CO	134-35	55	50	$CHCl_3$/ Pet.ether	63.69 (63.65)	3.71 (3.74)
n	4- $CH_3C_6H_4CO$	112-14	60	50	C_6H_6	69.61 (69.98)	4.54 (4.51)
o	4-$CH_3OC_6H_4CO$	97-98	80	70	$CHCl_3$/ EtOH	66.28 (66.25)	2.27 (2.29)

Route A -ketone (13a) was used .

Route B -thioketone (13b) was used.

Table II.2 : Spectral data of 5-phenyl-3-arylidene-1,2-dithioles (14a-g)

Compound	IR data (KBr) Cm^{-1}			H-NMR ($CDCl_3$) data		
	$\nu C=C$	$\phi C-H$	$\nu C=O$	δ(ppm)	No.of protons	Assignment
1	2	3	4	5	6	7
14 a	1587	995	–	–	–	–
b	1585	970	–	–	–	–
c	1590	950	–	–	–	–
d	1600	975	–	7.20-8.20,m	9 H	aromatic
				7.16,s	1 H	olefinic
				7.19,s	1 H	olefinic
e	1592	971	–	7.36-7.90,m	9 H	aromatic
				7.27,s	1 H	olefinic
				7.34,s	1 H	olefinic
f	–	–	–	7.52-8.50,m	9 H	aromatic
				7.40,s	1 H	olefinic
				7.44,s	1 H	olefinic
g	1605	935	–	7.22-8.00,m	9 H	aromatic
				7.14,s	1 H	olefinic
				7.20,s	1 H	olefinic
				2.38,s	3 H	CH_3

Table II.2 (Contd.)

1	2	3	4	5	6	7
14h	–	–	–	7.20-8.10,m	9 H	aromatic
				6.82,s	1 H	olefinic
				7.00,s	1 H	olefinic
				3.83,s	3 H	OCH_3
i	–	–	–	7.38-7.93,m	12 H	aromatic
				7.33,s	1 H	olefinic
				7.35,s	1 H	olefinic
j	1633	995	–	–	–	–
k	–	–	–	–	–	–
l	1612	998	1662	–	–	–
m	1610	933	1658	–	–	–
n	–	–	–	7.30-8.10,m	9 H	aromatic
				7.23,s	1 H	olefinic
				7.25,s	1 H	olefinic
				2.40,s	3 H	CH_3
o	–	–	–	7.04-8.13,m	9 H	aromatic
				6.78,s	1 H	olefinic
				6.93,s	1 H	olefinic
				3.83;s	3 H	OCH_3

φ=out of plane deformation of hydrogen attached to C=C ; s = Singlet, m = multiplet, ν=vibration stretching

CHAPTER III

STUDIES ON A NEW PHOSPHONATE CARBANION*

III.1 ABSTRACT

A new dimethyl 2,7-dichloro-9-fluorenylphosphonate cabanion (2) has been generated 'in situ' and reacted with a series of aromatic aldehydes to give exocyclic olefins, 9-arylidene -2,7-dichlorofluorenes (4a-t) in good yields. The reaction of dimethyl 2,7-dichloro-9-fluorenylphosphonate carbanion (2) with isophthaldehyde and terephthaldehyde gives 1,3-bis (2,7-dichloro-9-fluorenylidene) xylene (4u) and 1,4-bis (2,7-dichloro-9-fluorenylidene) xylene (4v) respectively. The stuctural assignments of phosphonate (1) and the resulting products are based on spectral data. The phosphonate shows good antibacterial activity in soil.

III.2 INTRODUCTION

The phosphonate carbanion -a Wittig Horner reagent is especially valuable because of its enhanced nucleophilicity and good yield of the products. Sometimes these reagents are

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* A paper based on this work has been published in the Indian J. Chem.,25B, 1067 (1986).

found to react with ketone which have failed to react with corresponding phosphorane intermediate- "Wittig reagent". The reaction of phosphonate carbanion with carbonyl compounds to form olefins offers the most accessible route for the conversion of carbonyl compounds into their olefinic system because of its specificity and versatile nature for the introduction of double bond. The phosphonate carbanions are found to be better olefinting agents than the analogous phosphorane intermediates and afford products in better yields.[1-5] Prompted by this and in continuation of studies on the reactivity of phosphorus containing carbanions [6-9], we have described here the reactivity of a new dimethyl 2,7-dichloro-9-fluorenylphosphonate carbanion (2) towards various mono- and disubstituted benzaldehydes.

III.3 RESULTS AND DISCUSSION

The reaction of trimethylphosphite with 2,7-dichloro-9-bromofluorene at 150°C gave dimethyl 2,7-dichloro-9-fluorenylphosphonate (1) in 70% yield. Treatment of 1 with NaH in THF or benzene resulted in a exothermic reaction with the generation of a pinkish red colouartion indicating the formation of phosphonate carbanion (2). The carbanion (2) could not be isolated due to lack stability towards atmoshpheric components. Hence its structure (2) was evidence on the basis of its precursor (1). The NMR spectral data of the latter showed a characterstic doublet at 3.55 due to 6H of two methoxy groups.

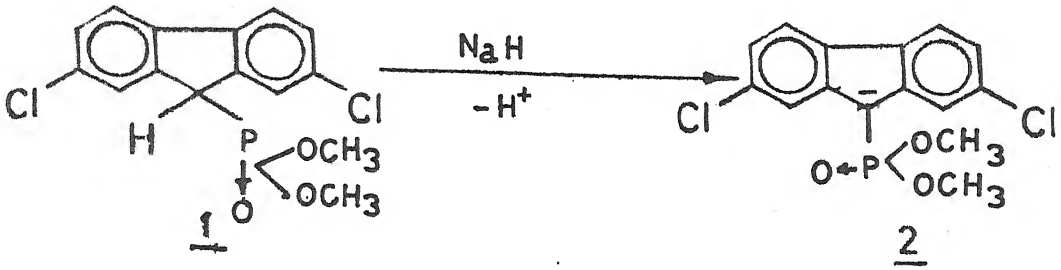
The proton attached to C_9 of fluorene ring was exhibited at δ4.55 (d;J_{PH} =22 Cps). The doublet of C_9- H was due to proton absorbed as multiplet in the range δ 7.25- 8.35.

The reaction of 2 with a series of substituted benzaldehyde (3a-r) was carried out at 100°C to afford 2,7-dichloro-9- (substituted benzylidene) fluorenes (4a-r) in 70-90% yields. A similar reaction of 2 with isophthaldehyde (3u) and terephthaldehyde (3v) gave 1,3-bis (2,7- dichloro-9-fluorenylidene) xylene (4u) and 1,4-bis (2,7-dichloro-9-fluorenylidene) xylene (4v) in 55-60% yields. The carbanion 2 also reacted with acetone (3s) and acetophenone (3t) to afford 2,7-dichloro-9-isopropylidene fluorene (4s)and 2,7-dichloro-9-(α-methylbenzylidene) fluorene (4t) respectively.

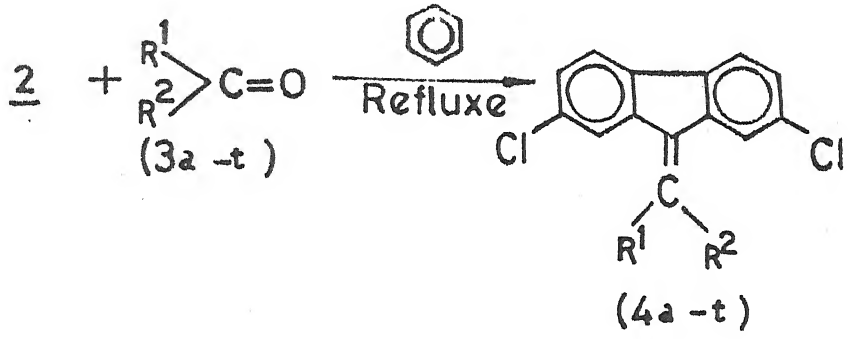
The carbanion (2) was found to be more reactive than the phosphorane intermediate[10]. It reacted smoothly with ketones unlike the coressponding phosphorane intermediate[10]. The enhanced nucleophilicty of (2) was attributed to the inductive effect of $(CH_3O)_2P=O$ group. The phosphonate carbanion (2) was also found to be more reactive than dimethyl-9-fluorenylphosphonate [11].

All the fluorenes (4a-v) synthesized gave satisfactory elemental analysis and spectral data. The melting points were in accordance with those reported in literature[12]. The IR spectra of (4a-v) exhibited characteristic absorption bands at 1630-1590 (C=C) and 990-960 (out-of-plane deformation of C-H of CH=C system). In the NMR ($CDCl_3$) spectra of (4) the olefinic protons appeared at δ6.55-7.25, the aromatic protons as a multiplet at

Scheme III ·1

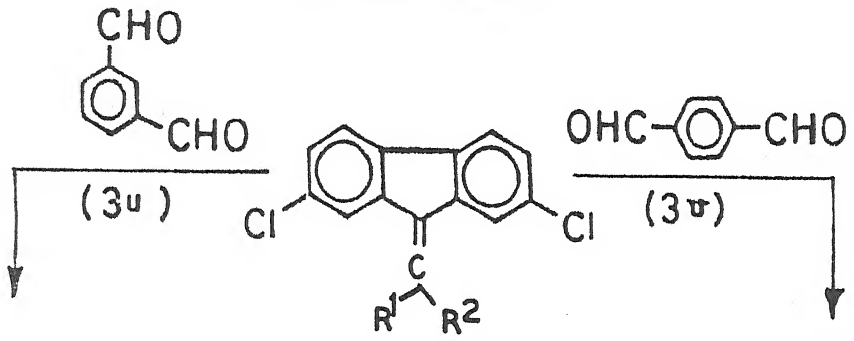


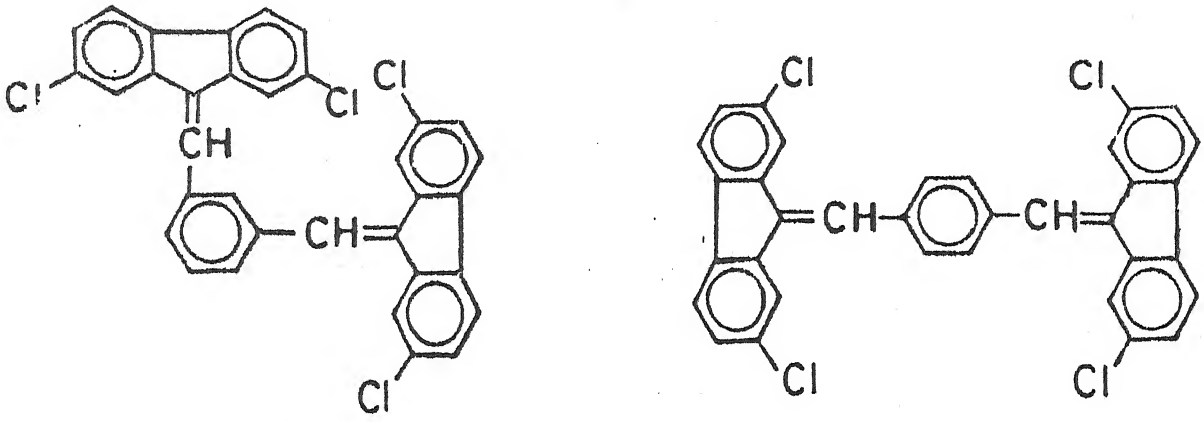
1 2



(4a -t)

Scheme III ·2





4u 4v

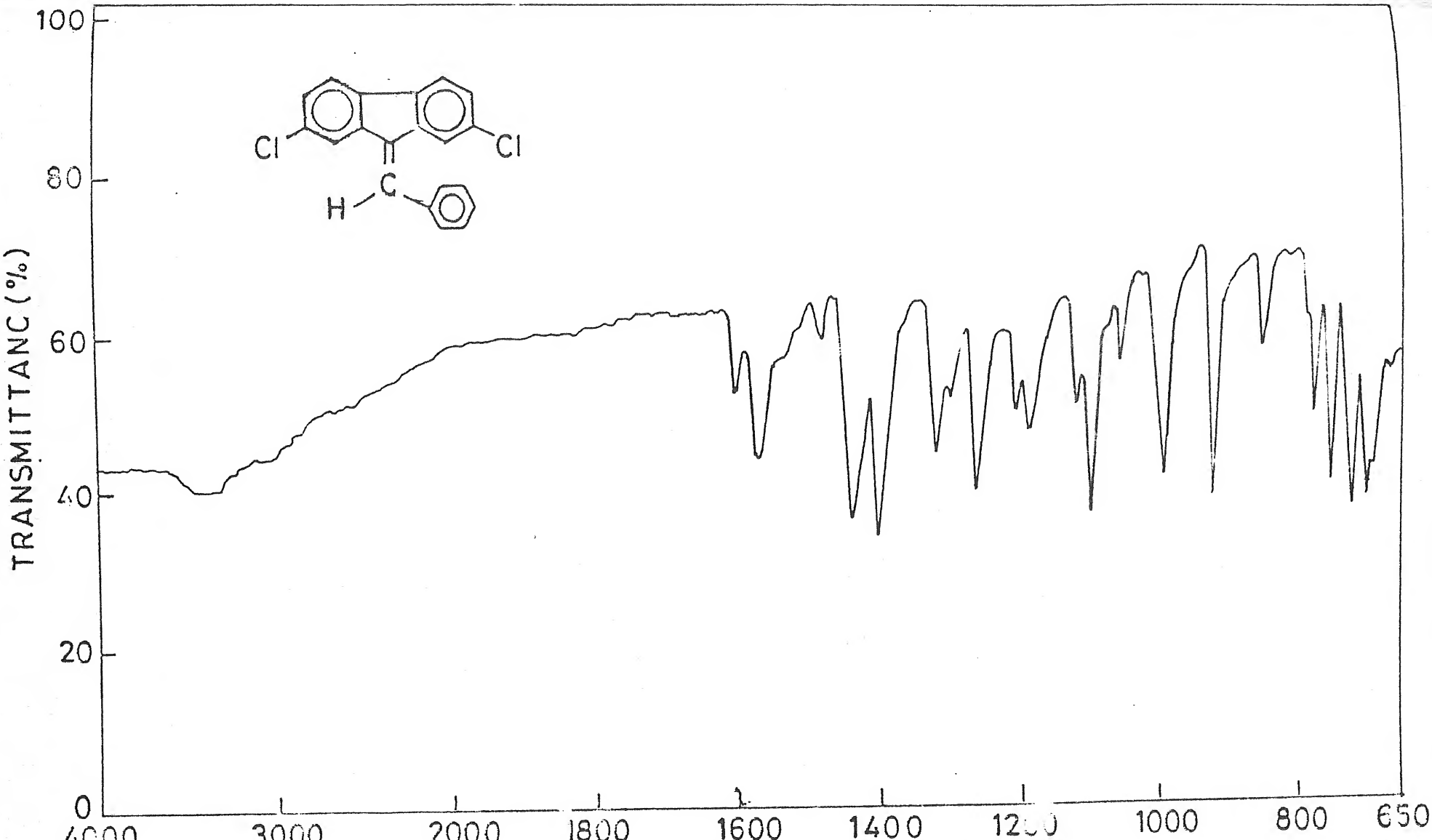
δ 6.55 – 8.35 and the aliphatic methyl and methoxy protons at 2.25 and 3.95, respectively.

The soil bacterial population was developed using Thornton's Agar media. The phosphate (1) was tested on the soil bacterial population using different concentrations of 2 (10,100,200,500 & 1000 ppm). The bacterial population was found to decrease with increasing concentration. The bactericidal activity of (2) was optimum at 1000 ppm concentration.

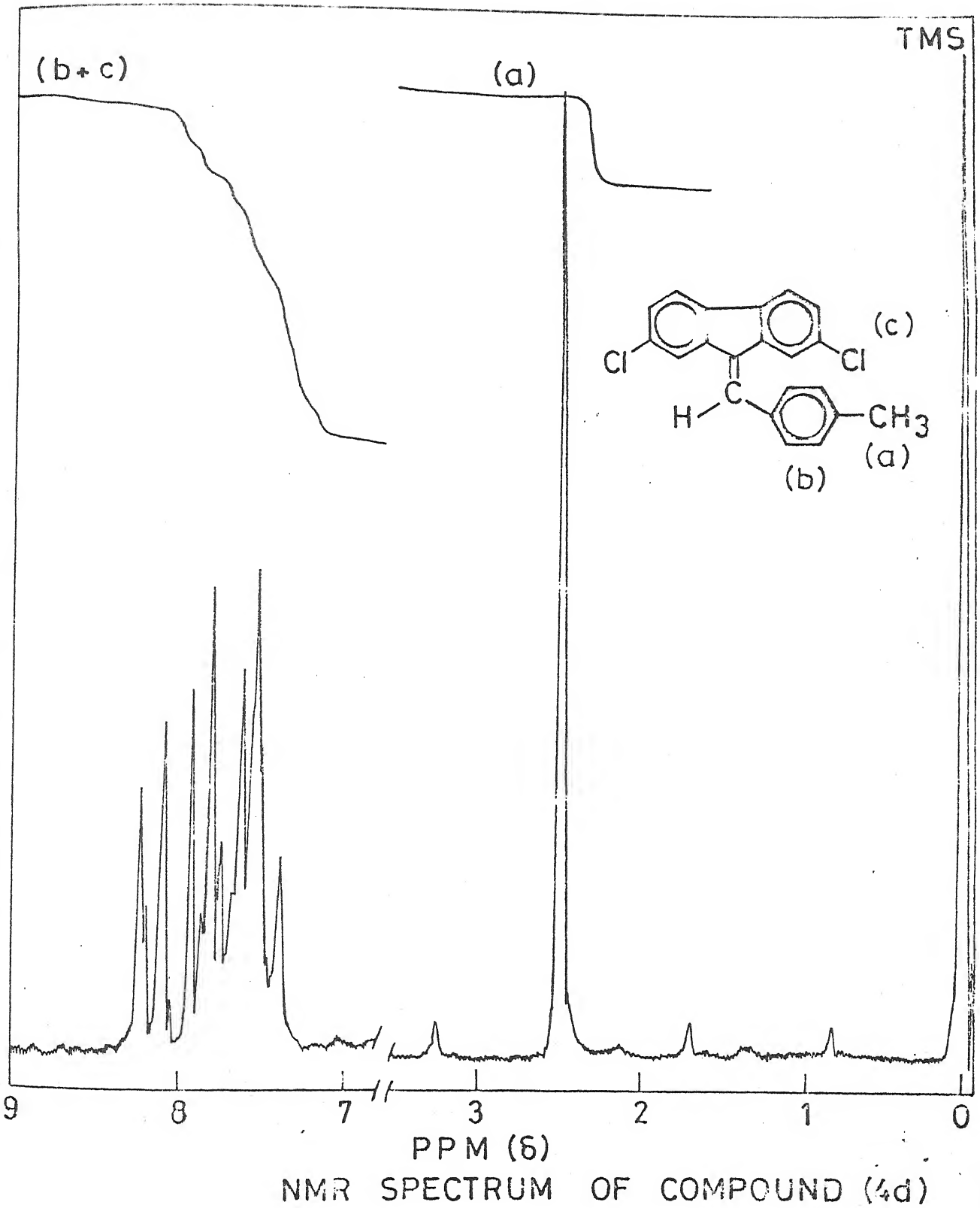
III. 4. EXPERIMENTAL

III.4.1 Starting Materials

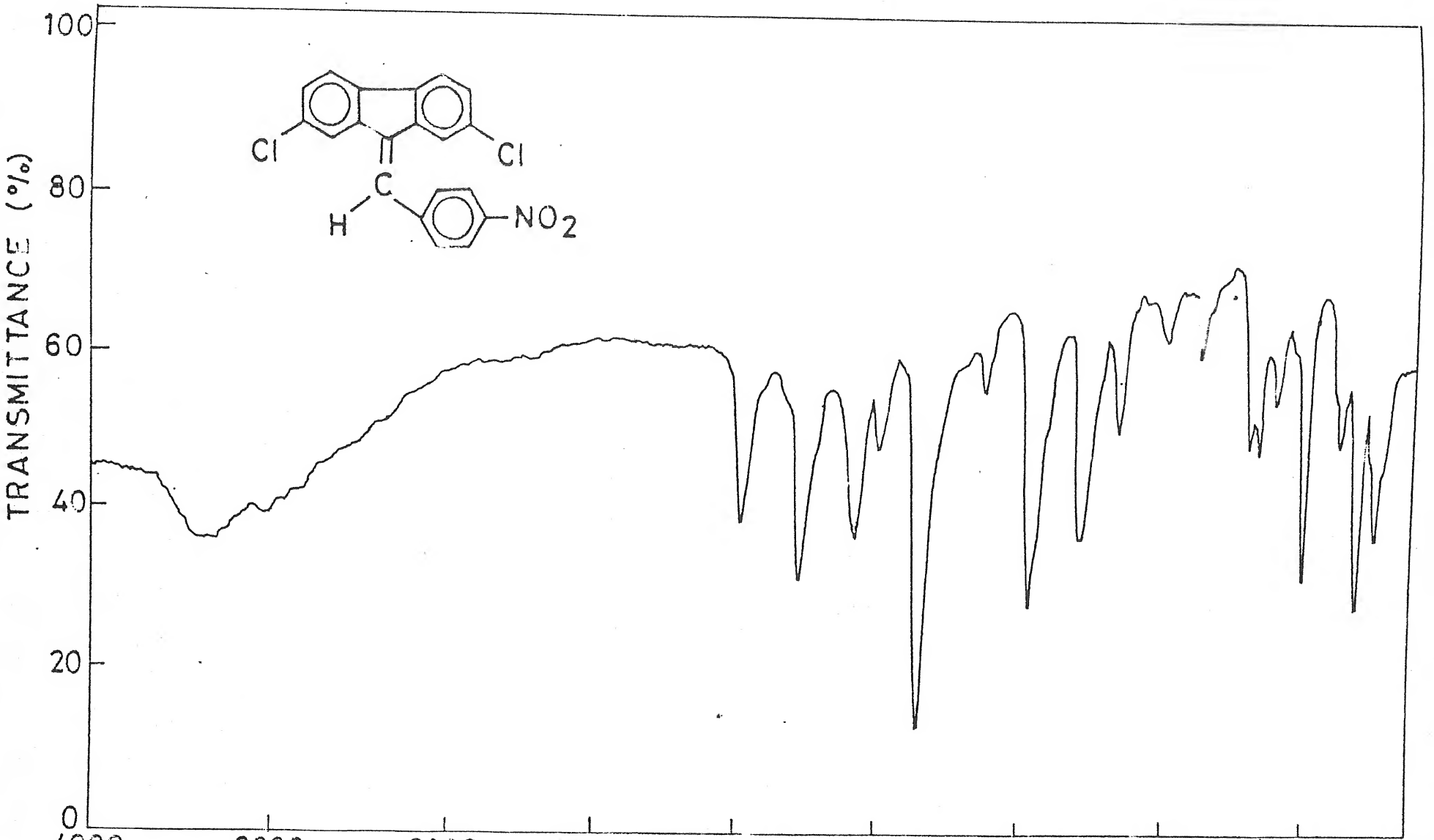
All the regents were obtained from commercial sources (BDH, E.Merck). Triphenylphosphites were purchased from SISCO laboratory. 2,7-dichlorofluorene was prepared by passing Cl_2 gas in $CHCl_3$ solution containing fluorene according to the procedure cited in literature.[12] 9-Bromo-2,7- dichlorofluorene dissolved in CCl_4 using benzoylperoxide as free radical generator. Melting points were determined on Gallen Kamp apparatus and are uncorrected. The IR spectra were recorded on a Perkin Elmer infracord spectrophotometer. The NMR spectra ($CDCl_3$) were recorded on a Varian A.60 spectrometer using TMS as an internal standard. The compounds were purified by columm chromatography over netural alumina. Purity was checked by TLC.



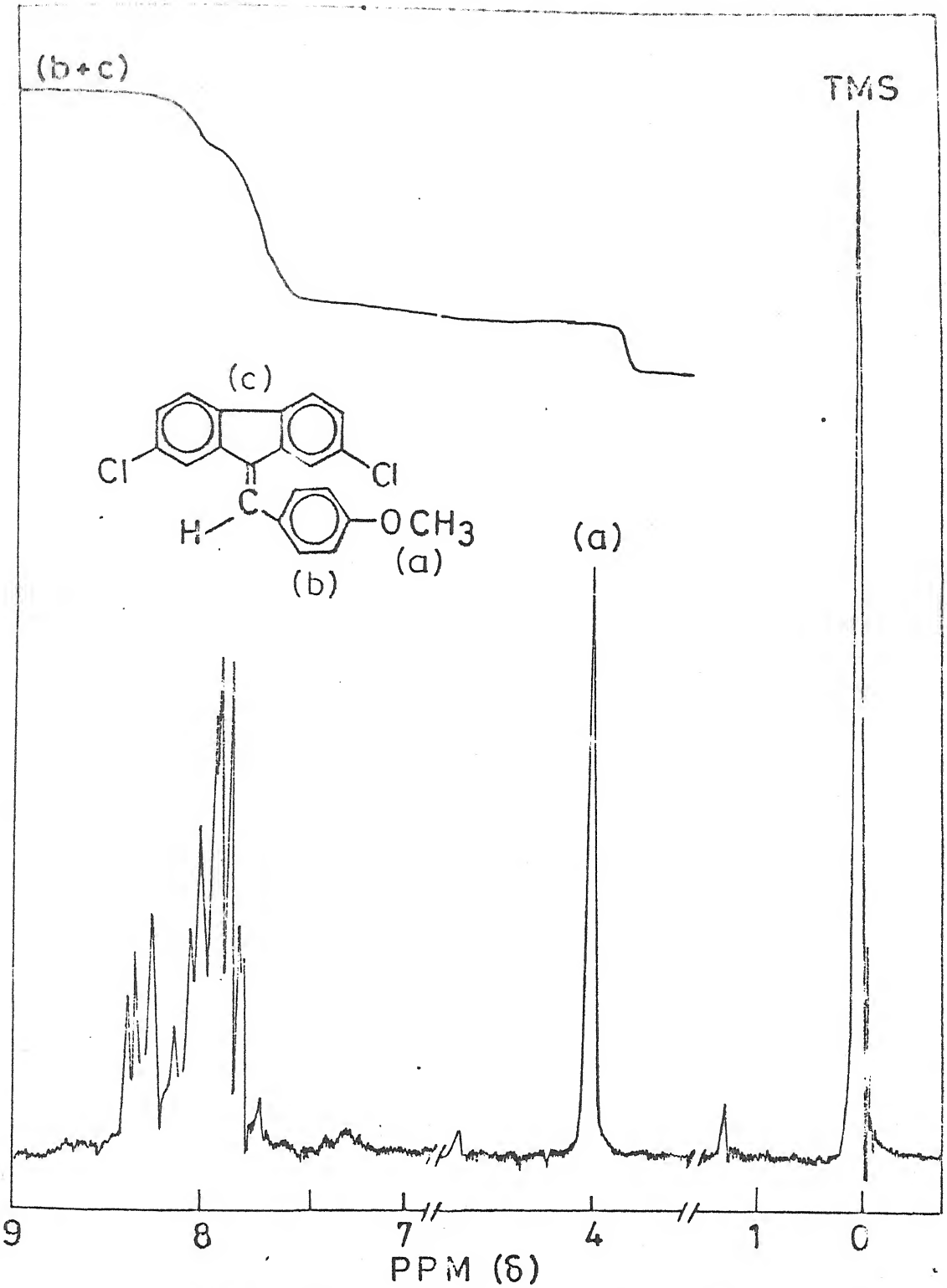
IR SPECTRUM OF COMPOUND (4a)



NMR SPECTRUM OF COMPOUND (4d)



IR SPECTRUM OF COMPOUND (4 j)



NMR SPECTRUM OF COMPOUND (4m)

III.4.2 Preparation of dimethyl 2,7-dichloro-9- fluorenyl-phosphonate (1)

A solution of trimethylphosphite (50 mmole) and 50 mmole of 9-bromo-2,7- dichlorofluerene was heated in an oil bath under nitrogen atmoshphere at 150°C for 16-18 hrs. . Methyl bromide produced in the reaction was distilled off in vaccuo and the residue extracted twice with ether . The ethereal layer on evaporation gave pink a compound which on recrystallization from n -hexane afforded pink crystals of (1), yield- 80%, m. p. -129-30°C.

Anal.data found : C, 52.5% ;H, 3.8% . Calcd. for $C_{15}H_{13}O_3PCl_2$ C, 52.5% ; H, 3.8% .

IR spectrum (KBr) :1315 cm $^{-1}$ (νP=O), 1035 cm $^{-1}$ (νP-O-C).

NMR spectrum ($CDCl_3$) : 3.58 (d, 6H, 2x OCH_3), 4.60 (d, 1H, C_9-H, J_{P-H} =20 H $_z$) and 7.28 -8.40 (m, 6H, Ar-H).

III.4.3 Reactions of dimethyl 2,7-dichloro-9-fluprenyl-phosphonate carbanion (2) with aromatic aldehydes (3a-r) and ketones (3s,t)

To a stirred suspension of dimethyl 2,7-dichloro-9-fluorenylphosphonate carbanion (2), generated from dimethyl 2,7-dichloro-9-fluorenylphosphonate (1) (5mmole) and sodium hydride (5 mmole) in THF (50 ml.), was added in an inert atmosphere (nitrogen) an appropriate aromatic aldehyde (5 mmole) and the mixture stirred at 100 °C for 4-10 hrs., then cooled to room temperature and excess of cold water added to it. The

precipitated solid mass was extracted with ether. The ethereal layer was dried (anhydrous sodium sulphate) and solvent removed under reduced pressure to give a solid mass which on column chromatography afforded 4. It was recrystallized from an appropriate solvent (Table III.1).

III.4.4 Reaction of dimethyl 2,7-dichloro-9-fluorenyl-phosphonate carbanion (2) with isophthaldehyde (3s) and terephthaldehyde (3t)

A mixture of 1 (8 mmole), sodium hydride (8 mmole) and (3s) or (3t) (4 mmole) in benzene (100 ml) was refluxed under nitrogen atmosphere for 12-14 hrs. The precipitate containing sodium hydride and unreacted phosphonate was removed and the filterate was concentrated on a steam bath under reduced pressure. The residue was chromatographed and the first fraction eluted with benzene- pet. ether (1 :2) gave 9-(3- aldehydobenzylidene)- 2,7-dichlorofluorene (4q) or 9-(4-aldehydobenzylidene)- 2,7-dichlorofluorene (4r) in 22-30% yield. The second fraction eluted with benzene afforded 1,3-bis (2,7-dichloro- 9-fluorenylidene) xylene (4u) or 1,4- bis (2,7-dichloro - 9-fluorenylidene) xylene (4v) in 50% and 55% yields respectively.

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Table III.1. Physical properties of 9-arylidene-2,7-dichlorofluorenes (4 a-t), 1,3-bis (2,7-dichloro-9-fluorenylidene) xylene (4u) and 1,4-bis (2,7-dichloro-9-fluorenylidene)xylene (4v).

Compd.	R^1	R^2	yield (%)	Recryst. solvent	m.p. (°C) (lit.m.p.) (°C)	Analysis found/ (calcd.) (%) C	H
1	2	3	4	5	6	7	8
4 a	H	C_6H_5	65	AcOH	92-93	74.2	3.7
					(94-95)[12]	(74.3)	(3.7)
b	H	2-$CH_3C_6H_4$	90	$CHCl_3$	140-42	74.7	3.1
					(142-43)[12]	(74.8)	(3.2)
c	H	3-$CH_3C_6H_4$	67	$CHCl_3$	95-97	74.7	3.2
					(96-97)[12]	(74.8)	(3.2)
d	H	4-$CH_3C_6H_4$	70	EtOH	145-47	74.8	3.1
					(148)[12]	(74.8)	(3.2)
e	H	2-ClC_6H_4	50	AcOH	155-57	67.1	3.0
					(159-60)[12]	(67.4)	(3.1)
f	H	3-ClC_6H_4	60	EtOH	130-32	67.2	3.0
					(134-35)[12]	(67.1)	(3.1)
g	H	4-ClC_6H_4	70	EtOH	202-03	67.2	3.1
					(204-05)[12]	(67.1)	(3.1)

1	2	3	4	5	6	7	8
4s	CH_3	CH_3	45	$CHCl_3$	88-90	70.2	4.3
						(70.2)	(4.4)
t	CH_3	C_6H_5	50	AcOH	130-32	74.1	4.2
						(74.0)	(4.2)
u	--	--	55	AcOH	255-56	65.1	2.8
					(253-54)[12]	(65.2)	(2.8)
v	--	--	60	AcOH	286-88	65.2	2.9
					(285)[12]	(65.2)	(2.9)

Table III.2 Spectral data of 9-arylidene-2,7-dichlorofluorenes (4a-t); 1,3-bis (2,7-dichloro-9-fluorenylidene) xylene (4 u) and 1,4-bis (2,7-dichloro-9-fluorenylidene) xylene (4v)

Compd.	IR(KBr) data (Cm^{-1})		H-NMR ($CDCl_3$) data		
	νC=C	ϕC-H	δppm	No.of protons	Assignment
1	2	3	4	5	6
4a	1595	960	-	-	-
b	1605	964	2.35,s	3 H	CH_3
			7.25-8.30,m	11 H	Aromatic+olefinic
c	1600	966	2.32,s	3 H	CH_3
			7.20-8.35,m	11 H	Aromatic+olefinic
d	1602	970	2.42	3 H	CH_3
			7.28-8.35,m	11 H	Aromatic+olefinic
e	1608	966	-	-	-
f	1595	965	-	-	-
g	1599	969	-	-	-
h	1615	960	-	-	-
k	1590	955	-	-	-
l	1598	962	-	-	-
m	1618	958	3.95,s	3 H	OCH_3
			7.30-8.30,m	11 H	Aromatic+olefinic

Table III.2 (Contd.)

1	2	3	4	5	6
4n	1620	978	5.95,s	2 H	O_2CH_2
			6.85-8.25,m	10 H	Aromatic+olefinic
o	1610	980	-	-	-
p	1615	975	-	-	-
s	1610	978	2.05,s	6 H	$(CH_3)_2C=O$
			7.25-8.35,m	6 H	Aromatic+olefinic
t	1618	985	2.30,s	3 H	$-CH_3$
			7.30-8.30,m	11 H	Aromatic+olefinic
u	1605	975	-	-	-
v	1615	980	-	-	-

ν=stretching vibration of C=C ; φ=out of plane deformation of H attached exocyclic C=C ; s =singlet, m =multiplet

CHAPTER IV

EFFECT OF BULKY SIZE OF CARBONYL SYSTEMS ON THE BETAINE DECOMPOSITION OF SEMI STABILIZED ARSORANE INTERMEDIATE (ARSONIUM YLID)

IV. 1. ABSTRACT

Synthesis of olefins by the interaction of benzyl idenetriphenylarsoranes with 9-anthraldehyde and 2,7-dichloro-9-fluorenone using benzen-sodamide, chloroform-sodium hydride and methanol-sodium methoxide as solvent-base pairs have been studied. In all the cases olefins are formed exclusively with good yield. Change in the solvents and bases has no effect on the course of betaine decomposition formed by the nucleophilic attack of ylids on carbonyl systems.

IV .2 INTRODUCTION

The behaviour of arsorane intermediates with carbonyl compounds in unlike phosphorane intermediates which have been proved to be the exclusive carbonyl olefinating reagents regardless of the nature of substituents present on them. The reaction of arsorane intermediate with carbonyl compounds is not very slective and cannot be characterised as the carbonyl olefination reaction (Wittig Reaction)[1,2] . Based on the information available so for, arsorane intermediates appear to

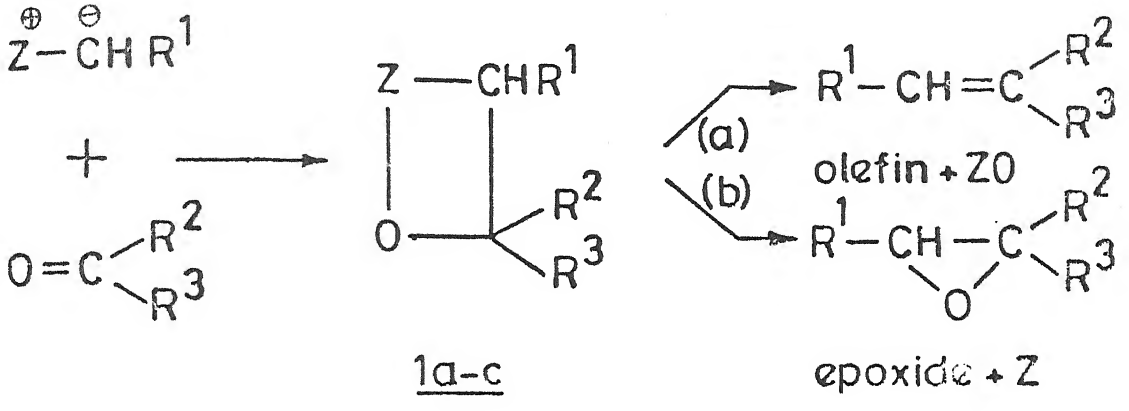
hald a position, intermediate between the phosphorane and sulfurane intermediates,in course of their reaction with carbonyl compounds. All the three types of intermediates (ylids) initially react indentically with carbonyl compounds to form a four membered cyclic transition betaine (I a-c). The decomposition of betaine (I a-c), which is dependent on the affinity of a particular heteroatom towards oxygen atom, dictates the exact course of reaction. Thus phosphonium betaine (Ia) follows path (a) involving the transfer of oxygen to the phosphorus because of the ability of latter to act as powerful oxygen scavanger, to give olefins and phosphine oxide.[1,2]. On the other hand,sulfonium betaine (Ib) follows path (b) involving displacement by the oxyanion on the carbon carrying sulfonium group, to afford epoxide exclusively [3] (Scheme IV.1).

Interestingly, the arsonium betaine (I c) can follow either path (a)or (b) or both depanding on the nature of substituents present on the ylidic carbanion. [4] For example, stabilized arsorane intermediates on their reaction with carbonyl compounds give olefins exclusively [5,6] while epoxides are the exclusive products of the reaction between non-stabilized arsorane intermediates and carbonyl compounds [7,8]. But since long time, there have been controversy regarding the exact course of reaction between semistabilized arsorane intermediates and carbonyl compounds giving either olefins or epoxide or both in the same reaction mixture. Johnson and Martin [9] were first to carry out the reaction of two semistabilized arsorane intermediates-

benzylidenetriphenylarsorane (IIa) and p-nitrobenzylidenetri pnenylarsorane (II b) with benzaldehyde (IIc,d) to give an equimolar amount of p-nitrostilbene (2) and p-nitrostilbeneoxide (3) (Scheme IV.2) Subsequent to this report, Nesmeyanov et al.[6] have, on the basis of their findings of the reaction between intermediate (II b) and benzaldehyde (II d), endorsed the same view as was given previously by Johnson et al[9], thus clearly establishing the dual character of semistabilized arsorane intermediates. Trippett et at.[4] have, for the frist time, succeded in establishing the factors which control the decomposition of the betaine, formed during the reaction between semistabilized arsorane intermediate and carbonyl compounds and have reported that the nature of substituent present on the benzylic portion of intermediate carbanion dictates the exact course of reaction . Thus p- substituted benzylidenetriphenylarsorane with p-substituted benzaldehyde to give olefins when benzylic p-substituent is strongly electron attracting, otherwise epoxides are formed and in no case, olefins and epoxide both are obtained, in contrast to the earlier observations of Johnson[9] and Nesmeyanov[6].

In addition to the structural factors [10,11] discussed above,Tewari et al.[12] have recently investigated that the decomposition of betaine intermediate is also markedly influenced by the nature of solvent and base used in the reaction between semistabilized arsorane intermediates and carbonyl compounds. Thus,benzylidenetriphenylarsorane (III a) and p-chlorobenzylidene

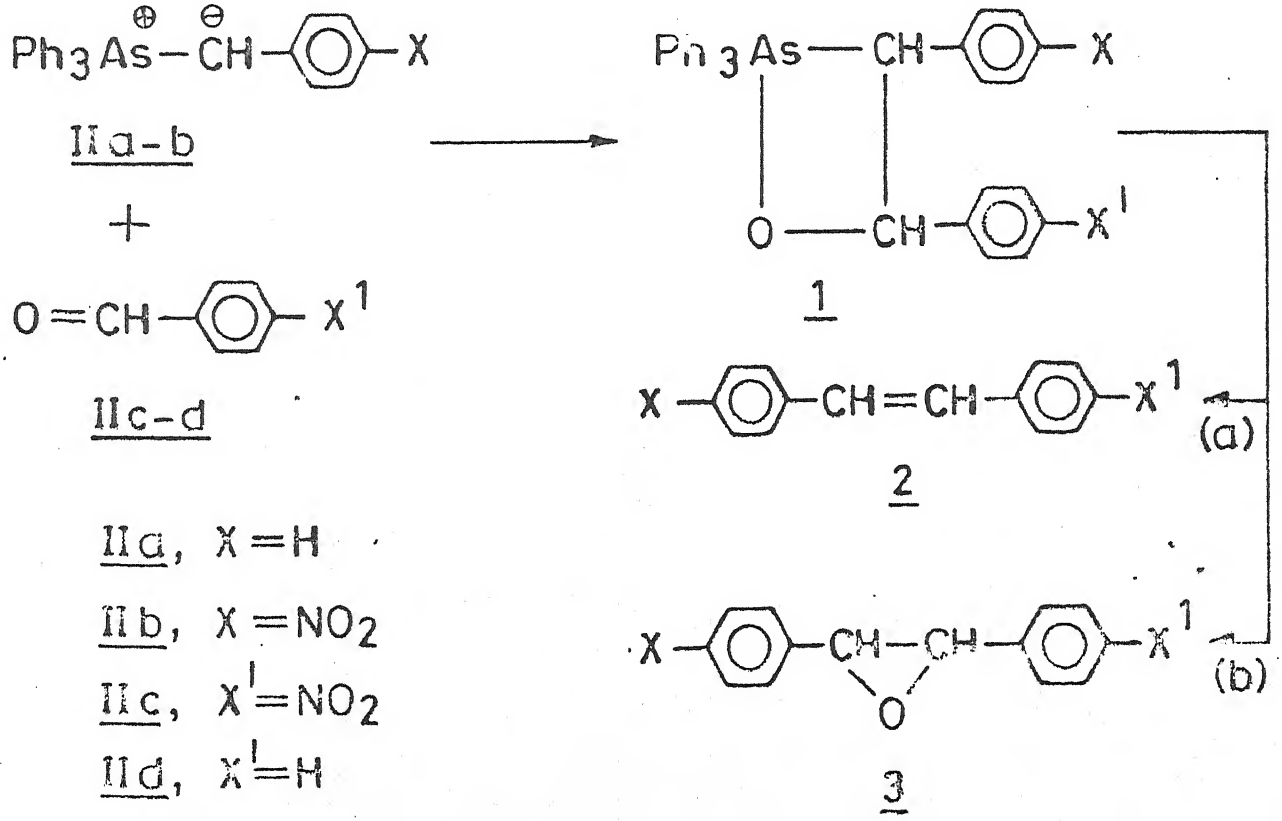
SCHEME IV·1



1a-c

Ia, Z = Ph_3P ; Ib, Z = Ph_2S
Ic, Z = Ph_3As

SCHEME IV·2



IIa, X = H
IIb, X = NO_2
IIc, X^1 = NO_2
IId, X^1 = H

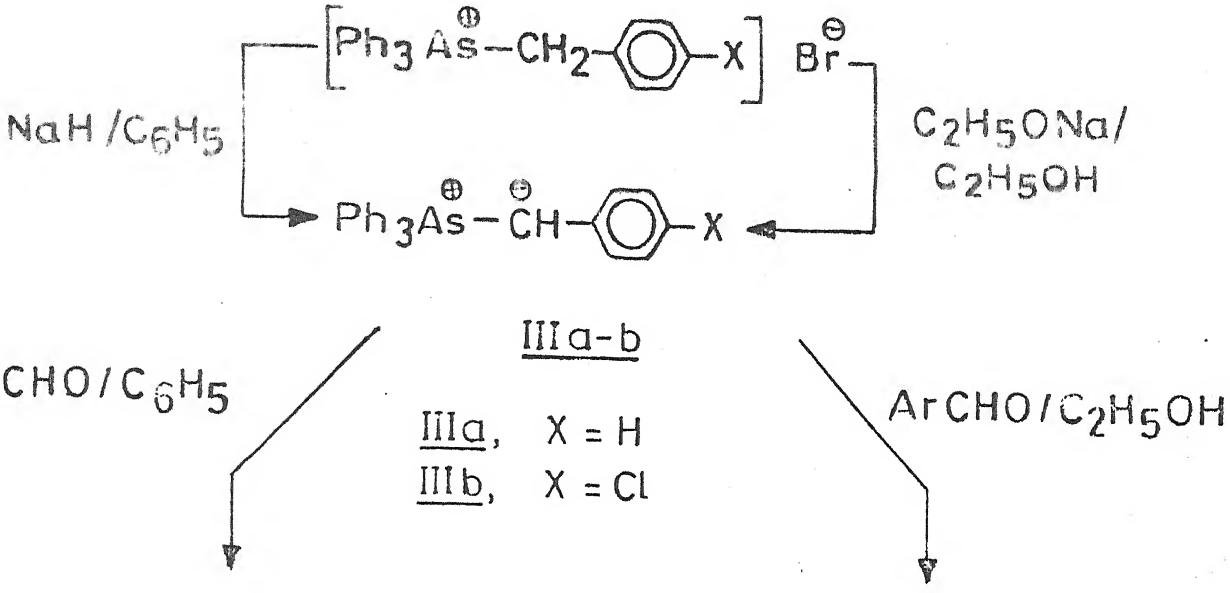
triphenylarsorane (III b) though carry electron donating group, when generated by the treatment of sodium hydride on their salt in benzene and reacted with substituted benzaldehyde give olefins (4) exclusively. When the intermediates (III a,b) are generated from their corresponding salts using sodium ethoxide in ethanol and reacted with substituted benzaldehyde, epoxides (5) are found to be the exclusive products (Scheme IV.3).

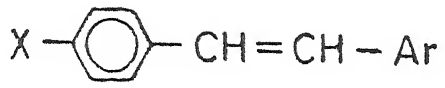
As a consequence of the above studies it was considered to be of great intreast to investigate the reactivity of a wide variety of semistabilized arsorane intermediates carrying electron donating as well as electron withdrawing substituents (2 a-i) towards the aldehyde (9-anthraldehyde) and ketone (2,7-dichloro-9-fluorenone) of bulky size in three different solvents and ylid- generating bases with a view to study the exact course of reaction as well as the effect of bulky size of carbonyl compounds and the variety of solvent-base pairs, in the decomposition of betaine (IV) and stereochemical nature of the resulting products.

IV. 3. RESULTS AND DISCUSSION

Quternization of triphenylarsine with substituted benzylbromides in benzene at reflux temperature gave substituted benzyl triphenylarsonium bromides (1 a-i) which on treatment with sodamide in benzene (Procedure A), or sodium hydride in chloroform (Procedure B), or sodium methoxide in methanol (Procedure C) developed intense colouration due to the formation

SCHEME IV·3





4

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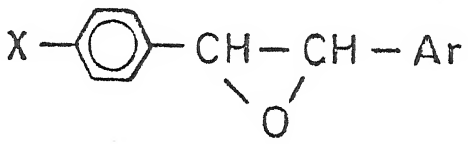
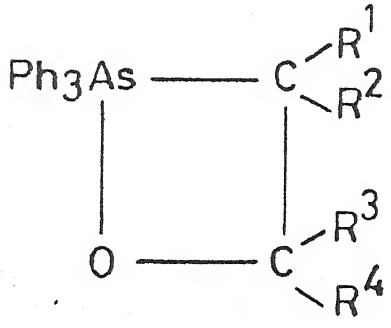
$Ph_3As=O$



5

\+

Ph_3As



IV

of arsorane intermediates, substituted benzylidenetriphenyl-arsorane (12 a-i) . These arsorane intermediate were not isolable due to the lack of stability under atmospheric conditions, hence their generation and reactions were carried out 'in situ'. The arsorane intermediates (12 a-i),generated from their salts (1a-i) in benzene with sodamide, on reaction with 9-anthraladehyde (8) and 2,7-dichloro-9-fluorenone (9) gave trans -1-(substituted phenyl)-2-(9-anthryl) ethylenes (3a-i) and 2,7-dichloro-9-substituted benzylidenefluorenes (4a- i) respectively in 40-70 % yields (Scheme IV. 5). Same products (3 a-i) and (4a-i) were obtained in 45-90 % yields when procedure B and C was employed instead of sodamide in benzene.

Thus ylid intermediates (2b — d) having electron attracting substituents with carbonyl system (8 & 9) favour the formation of olefins [(3b-d) & (4b-d)] exclusively in a manner analogous to phosphorane intermediates. The exclusive formation of olefins [(3b-d) & (4b-d)] by the ylid intermediates (2b-d) and non-availabity of epoxides are in accord with the observations of Trippett et al.[4]. However the reaction of ylid intermediate (2e-i) having electron donating substituents with carbonyl compounds (8 & 9) to form olefins [(3e-i) & (4e-i)] instead of the expected epoxide was contrary to the observations reported earlier [4]. Recently Tewari et al. have reported that the ylid intermediates with electron donating substituents gave olefins and epoxides in ethanol and benzene, respectively. In the present studies the reaction of ylid intermediates (2a-i) with

bulky carbonyl systems (8 & 9) in three different solvents gave exclusively the olefins in all the cases . This may probably be due to the bulky size of carbonyl compounds which facilitates the decomposition of betaine (IV) to give olefins only .

The exclusive formation of olefins and non-availability of epoxides from these ylid intermediates (2 a-i) are in accord with the behaviour analogus to phosphorane intermediate[13-15] and also consistent with the observations of Trippett et al.[4]

The mechanism and stereochemistry reported for stabilized and non- stabilized arsorane intermediates [4-7,10-12] were analogus to that of phosphorane intermediates. The ylid carbanions (2 a-i) attack on the carbonyl group to give a cyclic betaine having either threo-(7) or erythro-(6) configuration. The threo -(7) and erythro- (6) betains on decomposition gave trans- and cis- olefins, respectively[19-21] (Scheme IV.4). The threo betaine(7) which is more stable, thermodynamically than erythro -(6) is expected to dominate . Hence trans- olefins are formed as major products . The dominance of threo-betaine (7) may be due to bulky size of aldehyde (8) and ketone (9) and groups present on the ylid carbanion (2a-i) which were not eclipsed. The cis- olefins are not formed probably due to non stability of erythro-betaine(6), since there would be the interaction between anthracene or fluorenone ring of carbonyl compounds (8 & 9) and aryl group of ylid intermediates (2 a-i) . The erythro-betaine (6) being unstable undergoes conversion into threo-betaine (7)

via the formation of carbonyl compound and ylid intermediate as shown in scheme IV.4.

All the substituated ethylenes (3a-i) and fluorenes (4a-i) listed in Table (IV.1) gave satisfactory elemental analysis and their melting points were very close to those reported in literature.[15,23-25] The IR spectra of trans- ethylenes (3a-i) showed absorption band at 1615-1595 cm^{-1} (νC=C) and 965-940 cm^{-1}.The latter absorption bands are associated with out of plane deformation of hydrogen attached to carbon-carbon double bonds. The NMR spectra in general exhibited olefinic protons in the range δ 6.27-7.13 and aromatic protons at δ 6.50-8.40. The IR spectra of fluorene derivatives (4a-i) showed two bands in the range 1600-1585 cm^{-1} (νC=C) and 970 -950 cm^{-1}. The NMR spectra of fluorene derivatives exhibited exocyclic olefin protons in range δ7.00-7.15 and aromatic multiplet at 7.15-7.95.

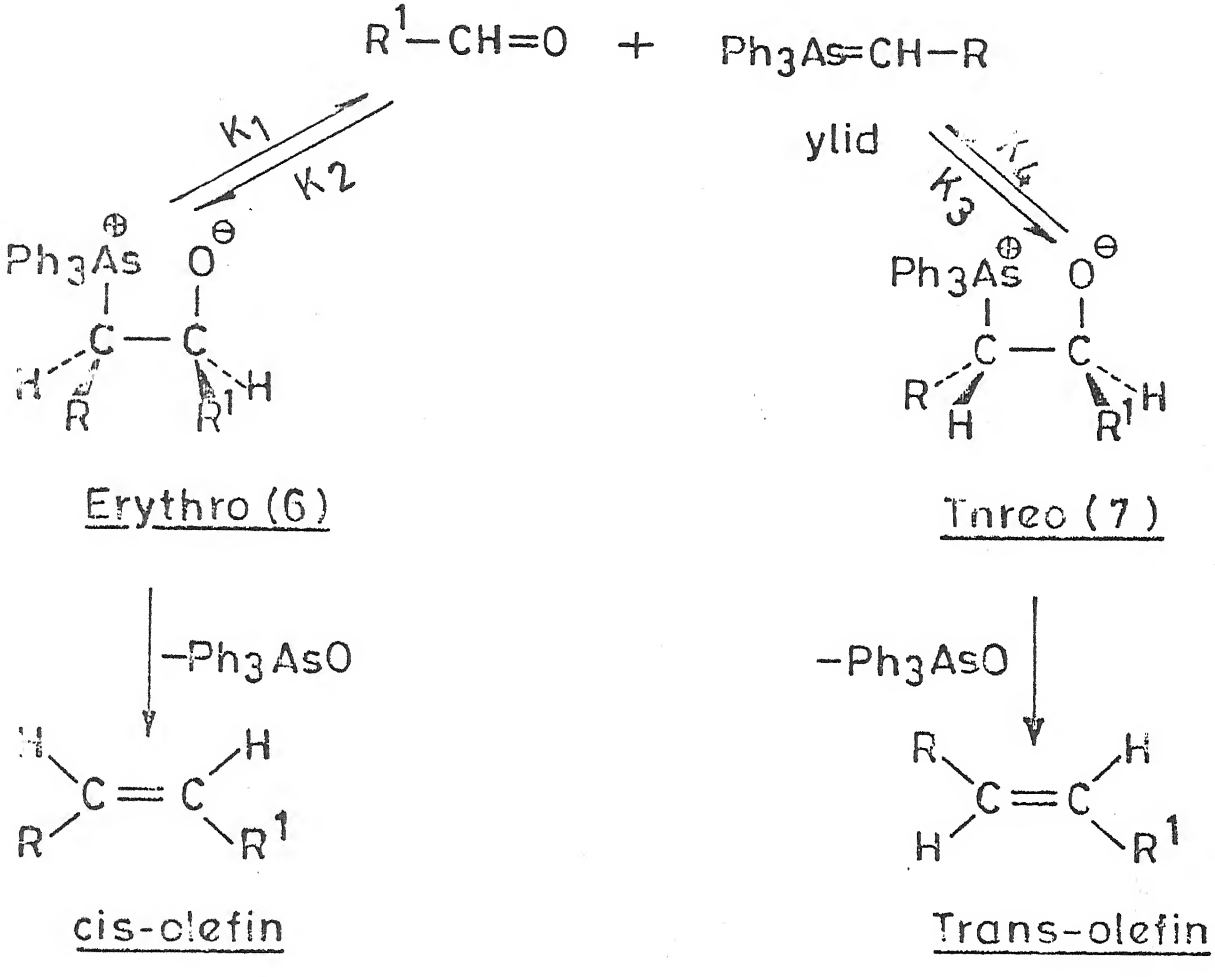
All the reactions were carried out under the atmosphere of nitrogen . All the products were purified by column chromatography over neutral alumina and their purity was checked by thin layer chromatography.

IV.4 EXPERIMENTAL

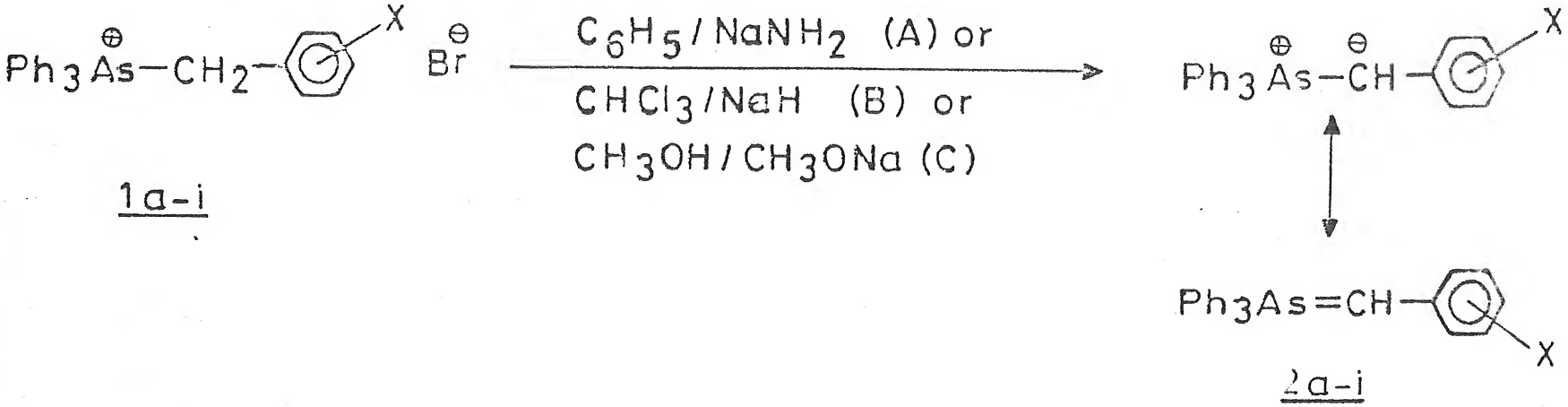
IV.4.1. Starting Materials

All the reagents were obtained from commercial sources (BDH, E.Merck and SISCO etc.). Starting materials were prepared according to the procedure cited in literature. All the unsubstituted and substituted benzyl bromides were prepared by

Scheme IV·4

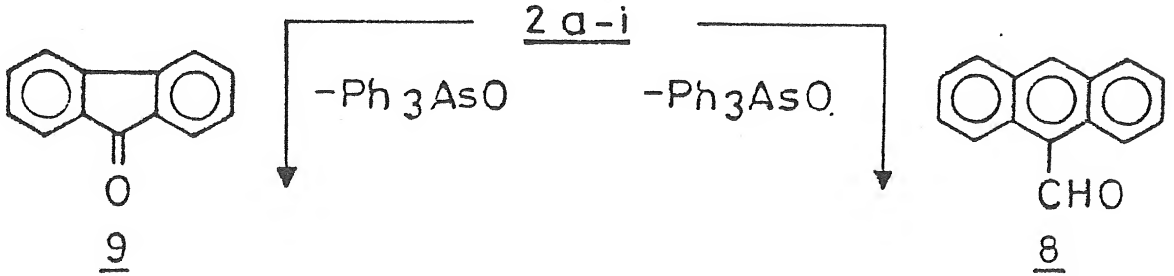

R1—CH=O + Ph3As=CH—R
ylid
K1
K2
K3
K4
Ph3As
O
Erythro (6)
Threo (7)
–Ph3AsO
–Ph3AsO
cis-olefin
Trans-olefin

SCHEME IV-5



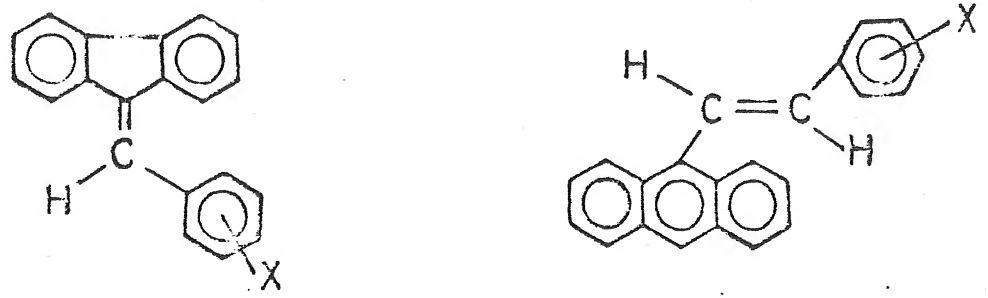
1a-i

2a-i



9

8



4a-i

3a-i

the bromination of toluene and substituted toluenes respectively, in carbon tetrachloride with N-bromosuccinimide in presence of benzoylperoxide, by refluxing the mixture for 5-7 hrs.. After refluxing, the remaining carbon tetrachloride was distilled off and remaining solid mass was washed with benzene, dried and recrystallied.

IV.4.2 Preparation of substituted benzyltriphenylarsonium bromide (1a -i)

All the arsonium salts (1a-i) were prepared as per procedure reported in literature.[10-13,22-29] For the preparation of arsonium salts (1a-i), a solution of triphenylarsine (50 mmole) and unsubstituted or substituted benzyl bromide(50 mmole) in 50 ml. of benzene was allowed to reflux on water bath for 4-6 hrs. A solid mass was precipitated which was filtered, dried and recrystallized twice from suitable solvents to give white shining crystals of unsubstituted and substituted benzyltriphenylarsonium bromides (1a-i).

IV.4.3 General procedure for preparation of olefins (3 a- i) & (4 a- i)

IV.4.3.1 Procedure A

To the stirred solution of ylid intermediate (2a-i), generated from their salts (1a-i) (4 mmole) with sodamide (5 mmole) in anhydrous benzene (100 ml), was added dropwise a solution of the carbonyl compound (8 & 9) (4 mmole) in benzene

(20 ml.) for 30 minutes. The reaction mixture was stirred at the room temperature for 6-8 hrs. The mixture was cooled and the residue containing triphenyloxide and unreacted sodamide was filtered. The filterate was concentrated on a steam bath under reduced pressure to give solid mass which was chromatographed using pet. ether (40-60°C)- benzene (1:4) as eluent to give the desired products. These products were recrystallized from appropriate solvent listed in Table IV. 1 .

IV.4.3.2. Procedure B

To a mixture of salts (1 a-i) (4mmole) and sodium hydride (5mmole) in chloroform (100 ml.) was added with stirring a solution of aldehyde (8) or ketone(9) in chloroform (20 ml.). The reaction mixture was stirred at the room temperature for 2 hrs., at 60°C for 5-8 hrs and then cooled and removed the excess solvent. The residue was filtered off and chromatographed as above to get the olefins.

IV 4.3.3. Procedure C

To a solution of ylid intermediate (2a-i) (4 mmole), generated from their salt (1a-i), with sodium methoxide (5 mmole)in dry methanol (150 ml.), was added aldehyde (8) or ketone (9) (4 mmole) and the reaction-mixture stirred at room temperature for 4-8 hrs.. The precipitate, thus obtained was filtered off, washed, dried and then subjected to chromatography as in procedure A.

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Table IV.1 Physical Properties of Trans-1- (substituted phenyl)-2-(9-anthryl)-ethylene (3a-i) and 9-arylidene-2,7-disubstituted fluorenes (4a-i)

Compd.	X	Y	Route	yield (%)	m.p. (°C) (Lit. m.p.) (°C)	Recryst. solvent	Analysis found/ (cald.) % C	H
1	2	3	4	5	6	7	8	9
13a	H	-	A	60	128-29	EtOH	94.25	5.75
			B	65	127-28	EtOH	94.30	5.73
			C	75	130-131	EtOH	94.26	5.74
					(130-32)[13]		(95.28)	(5.72)
b	2-NO_2	-	A	70	100-02	AcOH	81.21	4.60
			B	72	98-99	AcOH	81.20	4.62
			C	80	101-04	AcOH	81.24	4.64
					(100-01)[13]		(81.23)	(4.62)
c	3-NO_2	-	A	65	162-63	EtOH	81.24	4.64
			B	70	164-65	EtOH	81.22	4.66
			C	82	161-62	EtOH	81.20	4.63
					(160-62)[13]		(81.23)	(4.62)

1	2	3	4	5	6	7	8	9
3d	4-NO_2	--	A	70	220-22	EtOH	81.21	4.65
			B	76	222-23	EtOH	81.24	4.67
			C	90	223-24	EtOH	81.20	4.61
					(220-22)[13]		(81.23)	(4.62)
e	4-Cl	-	A	60	134-36	AcOH	83.92	4.73
			B	68	135-37	AcOH	83.93	4.74
			C	75	136-38	AcOH	83.95	4.75
					(135-36)[13]		(83.94)	(4.76)
f	4-Br	-	A	65	171-73	EtOH	73.50	4.19
			B	70	170-71	EtOH	73.55	4.20
			C	78	173-74	EtOH	73.48	4.15
					(172-74)[13]		(73.53)	(4.18)
g	4-I	-	A	60	141-43	AcOH	62.61	3.66
			B	67	140-41	AcOH	62.58	3.70
			C	75	144-45	AcOH	62.66	3.64
					(140-42)[13]		(62.63)	(3.69)
h	4-CH_3	-	A	68	150-52	AcOH	93.85	5.11
			B	72	148-49	AcOH	93.80	5.19
			C	80	153-54	AcOH	93.90	5.10
					(150-51)[13]		(93.87)	(5.13)

Table IV.1 (Contd.)

1	2	3	4	5	6	7	8	9
3i	4-CH_3O	–	A	67	174-75	EtOH	89.01	5.83
			B	78	172-73	EtOH	89.05	5.80
			C	85	170-71	EtOH	89.00	5.86
					(175-77)[13]		(89.03)	(5.81)
4a	H	Br	A	38	96-98	AcOH	58.23	2.92
			B	42	95-97	AcOH	58.20	3.00
			C	60	100-01	AcOH	58.28	2.94
					(98-99)[30]		(58.25)	(2.91)
b	2-NO_2	Br	A	35	198-200	EtOH	52.54	2.40
			B	45	203-05	EtOH	52.50	2.45
			C	65	197-99	EtOH	52.55	2.42
					(201-02)[30]		(52.51)	(2.41)
c	3-NO_2	Br	A	45	156-57	EtOH	52.55	2.44
			B	50	153-55	EtOH	52.58	2.49
			C	60	152-54	EtOH	52.49	2.38
					(154-55)[30]		(52.51)	(2.41)
d	4-NO_2	Br	A	48	196-98	AcOH	53.58	2.40
			B	54	198-99	AcOH	52.60	2.35
			C	62	194-96	AcOH	52.48	2.45
					(195-96)[30]		(52.51)	(2.41)

Table IV.1 (Contd.)

1	2	3	4	5	6	7	8	9
4e	4-Cl	Br	A	42	209-11	AcOH	53.72	2.44
			B	48	213-14	AcOH	53.80	2.40
			C	58	212-14	AcOH	53.71	2.50
					(211-12)[30]		(53.75)	(2.46)
f	4-Br	Br	A	35	252-54	EtOH	48.83	2.27
			B	40	250-54	EtOH	48.90	2.20
			C	55	255-56	EtOH	48.85	2.31
					(252-53)[30]		(48.88)	(2.24)
g	4-I	Br	A	30	208-10	AcOH	44.64	2.08
			B	36	205-06	AcOH	44.58	2.10
			C	50	210-11	AcOH	44.69	2.01
					(207-08)[30]		(44.61)	(2.05)
h	4-CH_3	Br	A	35	136-38	AcOH	59.19	3.31
			B	41	142-43	AcOH	59.10	3.20
			C	53	135-37	AcOH	59.20	3.25
					(140-41)[30]		(59.15)	(3.28)
i	4-CH_3O	Br	A	30	132-34	EtOH	57.06	3.13
			B	38	130-32	EtOH	57.00	3.22
			C	49	134-35	EtOH	57.11	3.15
					(132-33)[30]		(57.01)	(3.17)

Table IV.2. Spectral data oftrans-1-(substitutedphenyl)-2-(9-anthryl) ethylene (3a-i) and 9-arylidene-2,7- disubstituted fluorene (4a-i).

Compd.	H-NMR(CDCl3) data			IR (KBr) data Cm^{-1}	
	δ(ppm)	No.of protons	Assignment	$\nu C = C$	$\phi C - H$
1	2	3	4	5	6
3a	–	–	–	1612	950
b	–	–	–	1608	965
c	6.50-7.95,m	13 H	aromatic	–	–
	6.27,d	1 H	olefinic		
	6.42,d	1 H	olefinic		
d	–	–	–	1595	952
e	–	–	–	1600	945
f	6.50-8.55,m	13 H	aromatic	1598	940
	6.27,d	1 H	olefinic		
	6.35,d	1 H	olefinic		
g	–	–	–	1600	960
h	7.40-8.48,m	13 H	aromatic	1600	940
	6.90,d	1 H	olefinic		
	7.13,d	1 H	olefinic		
	2.80,s	3 H	CH_3		

Table IV.2. Spectral data oftrans-1-(substitutedphenyl)-2-(9-anthryl) ethylene (3a-i) and 9-arylidene-2,7- disubstituted fluorene (4a-i).

Compd.	H-NMR(CDCl3) data			IR (KBr) data Cm^{-1}	
	δ(ppm)	No.of protons	Assignment	$\nu C = C$	$\phi C - H$
1	2	3	4	5	6
3a	-	-	-	1612	950
b	-	-	-	1608	965
c	6.50-7.95,m	13 H	aromatic	-	-
	6.27,d	1 H	olefinic		
	6.42,d	1 H	olefinic		
d	-	-	-	1595	952
e	-	-	-	1600	945
f	6.50-8.55,m	13 H	aromatic	1598	940
	6.27,d	1 H	olefinic		
	6.35,d	1 H	olefinic		
g	-	-	-	1600	960
h	7.40-8.48,m	13 H	aromatic	1600	940
	6.90,d	1 H	olefinic		
	7.13,d	1 H	olefinic		
	2.80,s	3 H	CH_3		

Table IV.2. (Contd.)

1	2	3	4	5	6
i	7.20-8.53,m	13 H	aromatic	1615	955
	6.93,d	1 H	olefinic		
	7.05,d	1 H	olefinic		
	3.87,s	3 H	OCH_3		
4c	-	-	-	1585	920
d	-	-	-	1600	960
e	-	-	-	1605	930
h	7.30-8.40,m	10 H	aromatic	-	-
	7.20,s	1 H	olefinic		
	2.42,s	3 H	CH_3		
i	7.38-8.08	10 H	aromatic	1613	955
	7.28,s	1 H	olefinic		
	3.91,s	3 H	OCH_3		

s = singlet

m = multiple

ν = streching vibration

d = doublet

φ = out-of-plane-deformation

CHAPTER V

REACTIONS OF BENZYLTRIPHENYLARSONIUM BROMIDE AND 4-NITROBENZYL-TRIPHENYLARSONIUM BROMIDE WITH α,β-UNSATURATED KETONES : SYNTHESIS OF SOME NEW 1,3-DISUBSTITUTED NAPHTHALENES AND 1,3,7-TRISUBSTITUTED NAPHTHALENES *

V.1 ABSTRACT

Benzyltriphenylarsonium bromide and 4-nitrobenzyl-triphenylarsonium bromide have been prepared by the interaction of benzyl bromide and 4-nitrobenzyl bromide with triphenylarsine in anhydrous benzene at reflux temperature. A series of new 1,3-diarylnaphthalenes and 1,3-diaryl-7-nitronaphthalenes are formed in quantitative yields when benzyltriphenylarsonium bromide and 4-nitro benzyltriphenylarsonium bromide react with a wide range of substituted benzylideneacetophenones in glacial acetic acid, in presence of anhydrous zinc chloride and sodium acetate as cyclization agents. The structures of new 1,3-diarylnaphthalenes and 1,3-diaryl-7-nitronaphthalenes have been established by elemental analysis and NMR spectral data.

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* Apart of the work has been published in Indian J. Chem. 24 B 312 (1986).

V.2 INTRODUCTION

From the literature it has been clear that the various sythesises of naphthalenes derivaitives were postulated from time to time. The yield of naphthalenes derivatives from these sythesis was poor because these synthesis involves several steps. Houseet al.[1,2] first synthesized 1,8-diphenylnaphthalene (3). He first synthesized an alcohol (2) by the interaction of 8-phenyl-$\Delta^{1,10}$ octal-1-one (1) phenylmagnesium bromide, which on dehydrogenation followed by dehydration with 2,3-dichloro-5,6-dicyanobenzoquinone in boiling benzene formed the desired product (3) (Scheme V.1). In this process the yield of the product was poor, because this process involved several steps to form the final product. These many steps have decreases the yield of the final product.

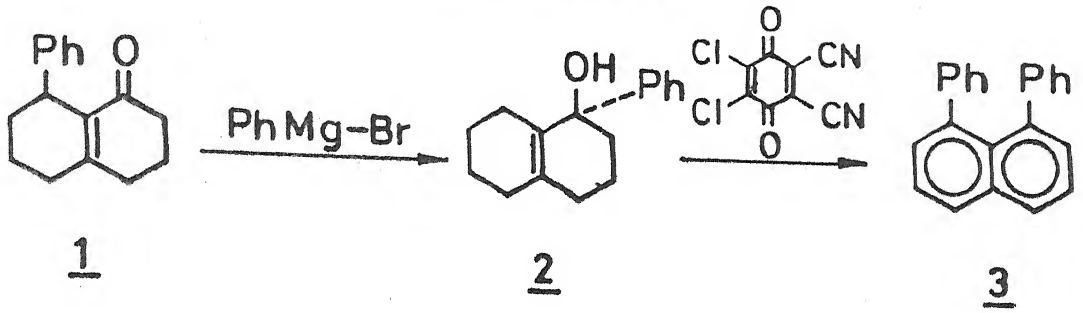
In the subsequent years, another attempts were made to get good yield of the final product. Hence an attractive route for the synthesis of substituted naphthalenes has been developed.[3] Thus starting from 1,4,5,8,9,10-hexahydro-1,4-dioxo-5-phenyl naphthalene (4), 1,8-diphenylnaphthalene (9) was synthesized. This process involved several steps as reduction of 4(5), thioketal formation (6), ethanolithioldesulfurisation with raney nickel (7), subsquent treatment of 7 with phenyl lithium to give 1-(trans)-hydroxy-cis-syn-1,8-diphenyldecaline (8) which on dehydrogenation with Pd/c (30%) yielded final product (9) (Scheme V.2)

The above route also involves many steps which reduce the yield of final product. Hence later Krohnke et al.[4], Tewari et al[5]

reported a convenient and facial route which involves single step and gives quantitative yield of the product. The above scienctists have synthesized 1,3-diphenylnaphthalene (12) by the interaction of benzalacetophenone (11) in presence of anhydrous zinc chloride (Scheme V.3). The superiorty of this method over aforementioned methods that it involved single step and gave better yield of desired product. Further more, this reaction allows selective introduction of substituents at 1 and 5 positions of the naphthalenes nucleus. However, only a few reactions, adopting this procedure have been reported and detailed experimental conditions have not been described. Prompted from this survey it seemed to be great interest to explore the domain of applicability of this new route.

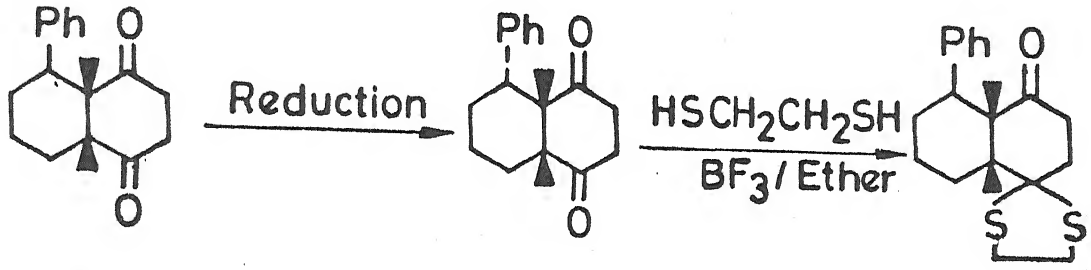
Recently Gupta et al.have reported the aza ring closure reaction of azomethine intermediates leading to the formation of pyridine nucleus .[6] Azomethine intermediates were utilized in the synthesis of a wide variety of acyclic[7,8] cyclic[9] and heterocyclic system[10-14]. In the present chapter we have reported a new carbocyclic reaction of azomethine intermediates involving the condensation of benzyltriphenylarsonium bromide and 4-nitro -benzyltriphenylarsonium bromide with various substituted benzylideneacetophenones in a mixture glacial acetic acid and sodium acetate using anhydrous zinc chloride as cyclization agent, with a view to investigate the applicability of this route in the synthesis of a wide range of naphthalene derivatives.

Scheme V·1



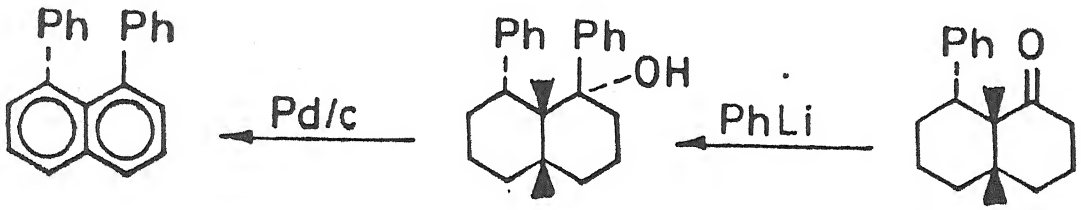
1 2 3

Scheme V·2



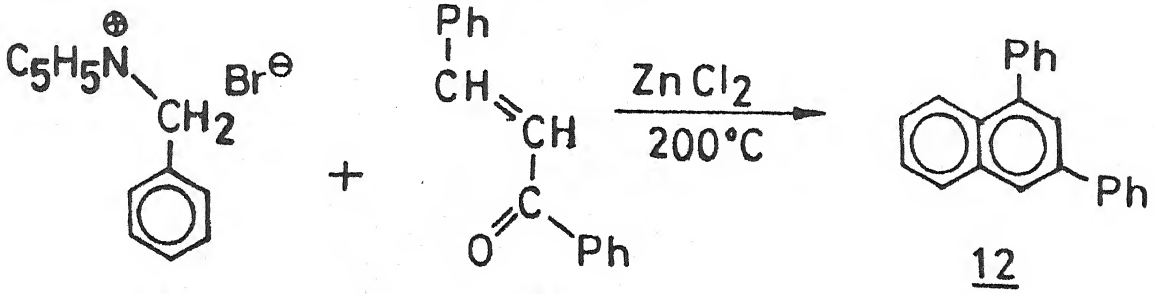
4 5 6

Raney Nickel ↓



9 8 7

Scheme V·3



10 11 12

V.4. RESULTS AND DISCUSSION

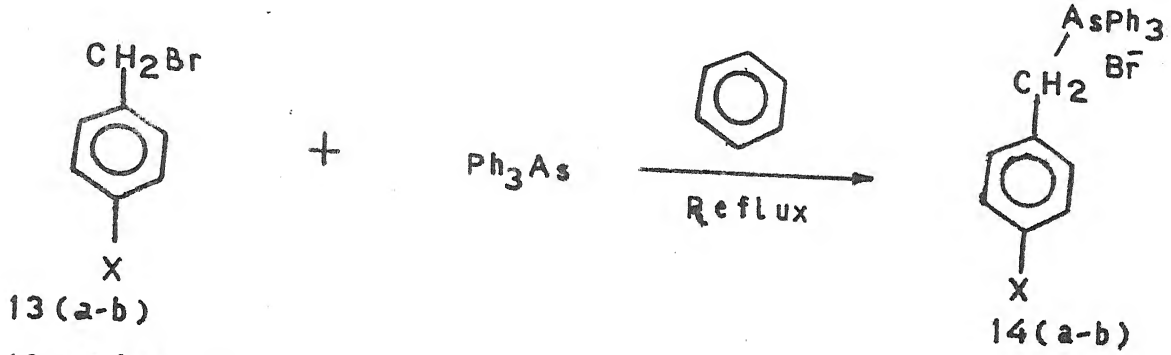
Quaternization of triphylarsine with benzyl bromide (13a) and 4-nitrobenzyl bromide (13b) in anhydrous benzene at reflux temperature gave benzyltriphenylarsonium bromide (14a) and 4-nitrobenzyltriphenylarsonium bromide (14b) respectively (Scheme V.4).

The structure of benzyltriphenylarsonium bromide (14a) and 4-nitrobenzyltriphenylarsonium bromide(14b) was confirmed on the basis of IR and NMR spectral data as reported in literature.[15]

The reaction of benzyltriphenylarsonium bromide (14a) and 4-nitrobenzyltriphenylarsonium bromide (14b) were carried out with a wide range of substituted benzylideneacetophenones in a mixture of sodium acetate and glacial acetic acid containing anhydrous zinc chloride under reflux temperature to afford 1,3-diaryl-naphthalenes (17a -j) and 1,3-diaryl-7-nitronaphthalenes (18a-g) respectively in 50-70% yields (Table V.1). It was , however observed that the yield of resulting naphthalenes were dependent upon the nature of substitutents attached to arsonium salts as well as to the α,β-unsaturated ketones. The reactivity of salt (14b) was lower than (14a)because of -I effect of NO_2 group which stabilized the carbanion formation . Hence, salt (14b) afforded lower yield of naphthalenes derivatives than salt (14a).

The reaction seems to procced via the intermediacy of a betaine type of derivatives (16) which is formed by the nucleophilic attack of ylid carbon (15a-b) presumabely generated 'in situ' by dehydrogenation of salt (13a-b), on the β-carbon of

Scheme V-4

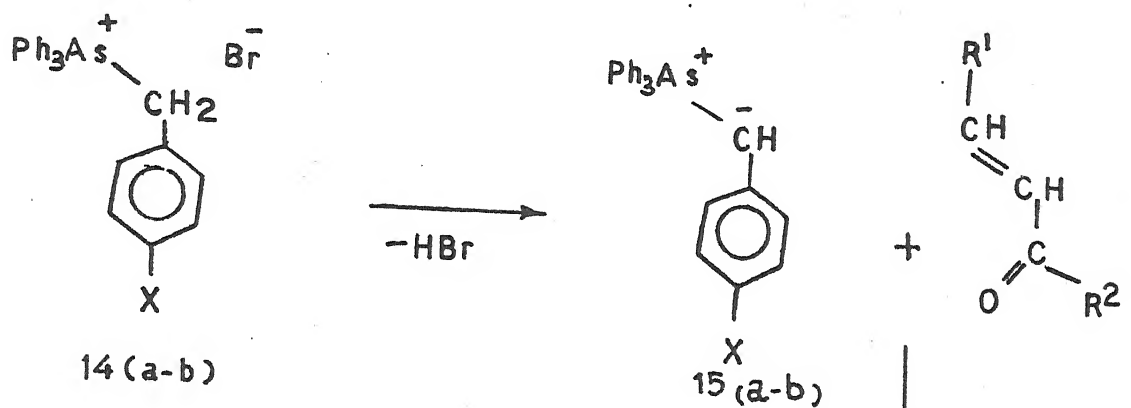


13 (a-b)

13 a & 14 a, x = H
b, x = NO2

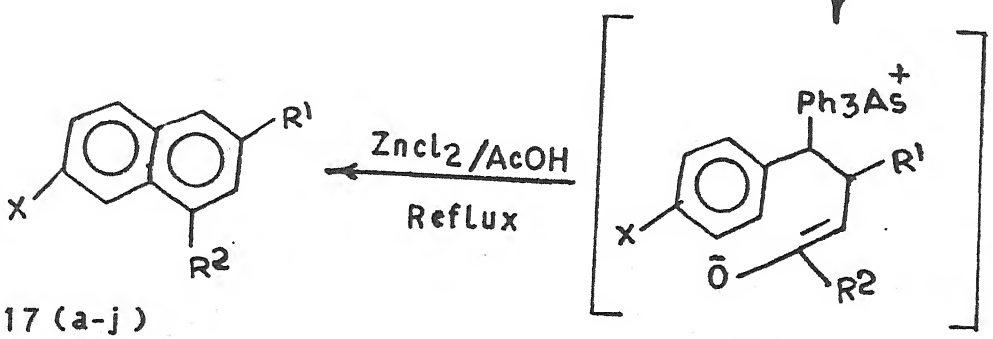
14 (a-b)

Scheme V-5



14 (a-b)

15 (a-b)



(16)

17 (a-j)
18 (a-g)

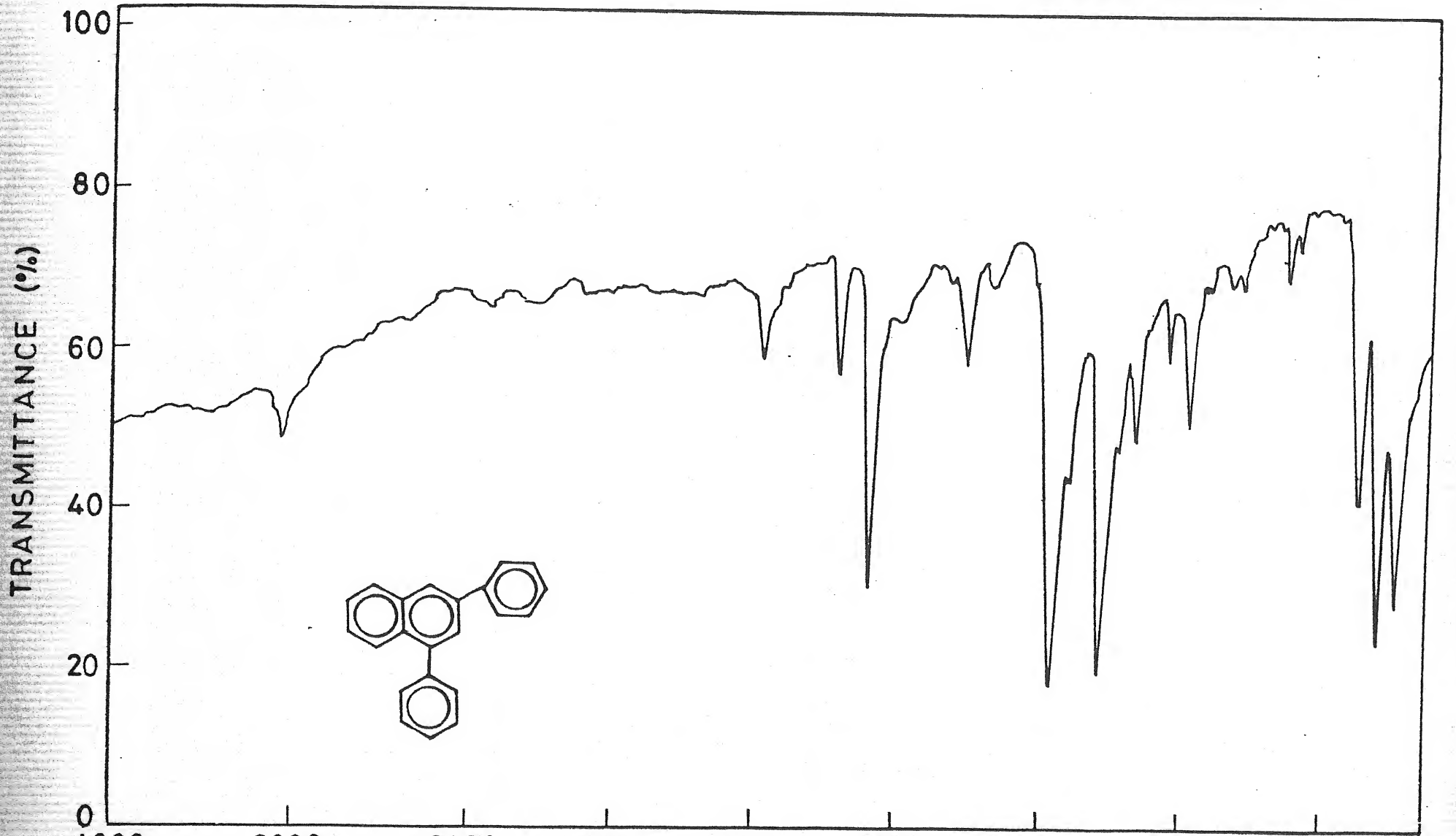
α,β-unsaturated ketone. Betaine (16), then undergoes cyclization in presence of anhydrous zinc chloride which is used as cyclization agent to afford naphthalene derivatives (17a-j) & (18 a-g) (Scheme V.5)

All naphthalenes obtained by this process were crystalline solids usually soluble in chloroform, benzene and acetone. The structure of 1,3-diarylnaphthalenes (17a-j) and 1,3-diaryl-7-nitronaphthalenes (18a-g) were established on the basis of elemental analysis. IR and NMR spectral data. All these compounds are new and gave satisfactory elemental analysis. All physical and spectral data have been shown in Table V.1 & 2. The IR spectra of these naphthalenes in general, exhibited a double absorption band around 1600 Cm $^{-1}$ which was assigned to the stretching vibrations of carbon-carbon double bond. The strong bonds in region 950-970 Cm^{-1} were diagnostic of absorption of polynuclear aromatics (out of plane deformation of hydrogen attached to carbon-carbon double bond). The NMR spectra of compound, in general exhibited aromatic multiplet in range δ6.50-8.40. The nitro group of the products showed a strong symmetrical stretching band at 1350-1330 Cm^{-1}.

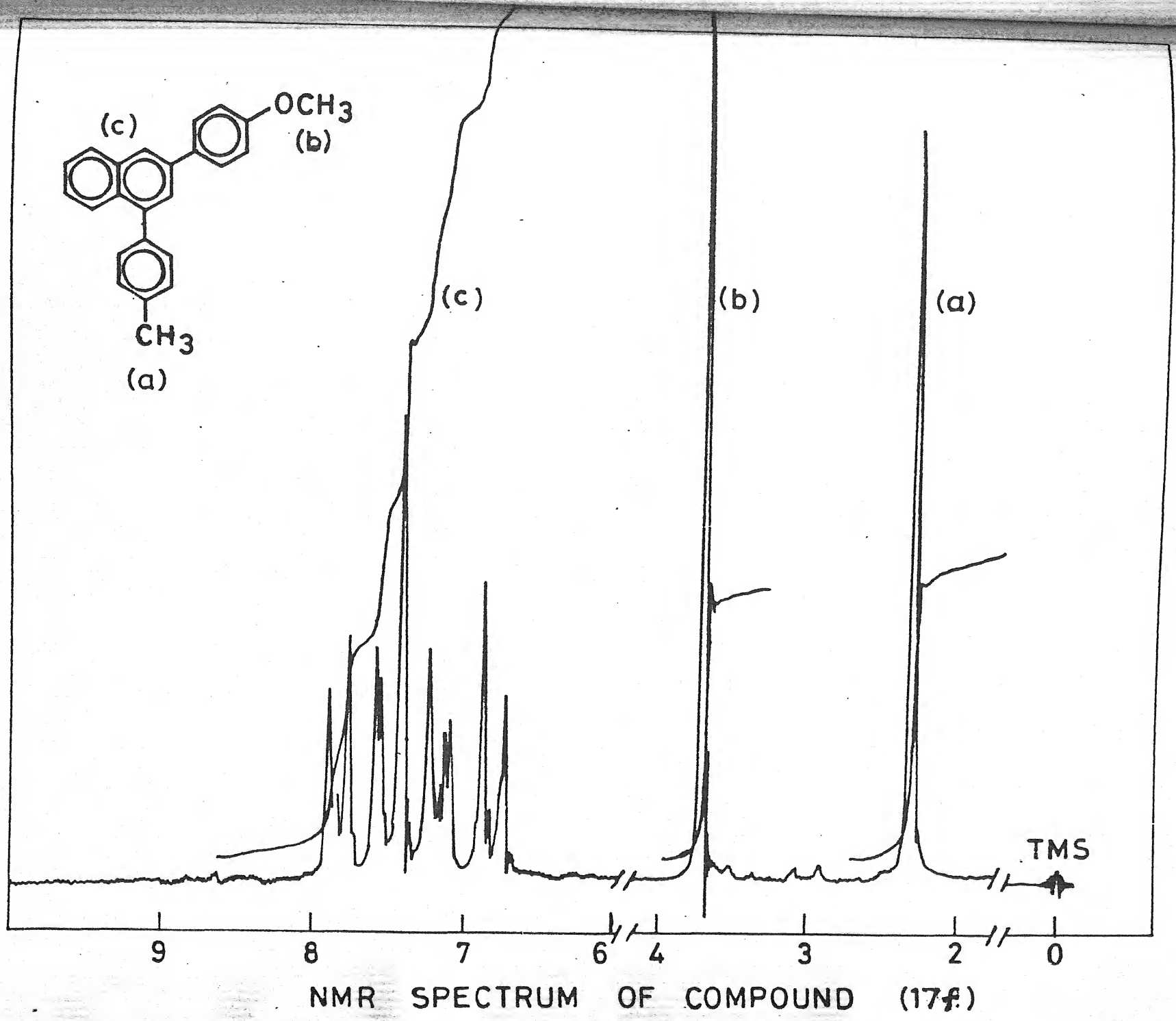
V.4. EXPERIMENTAL

V.4.1 Starting Materials

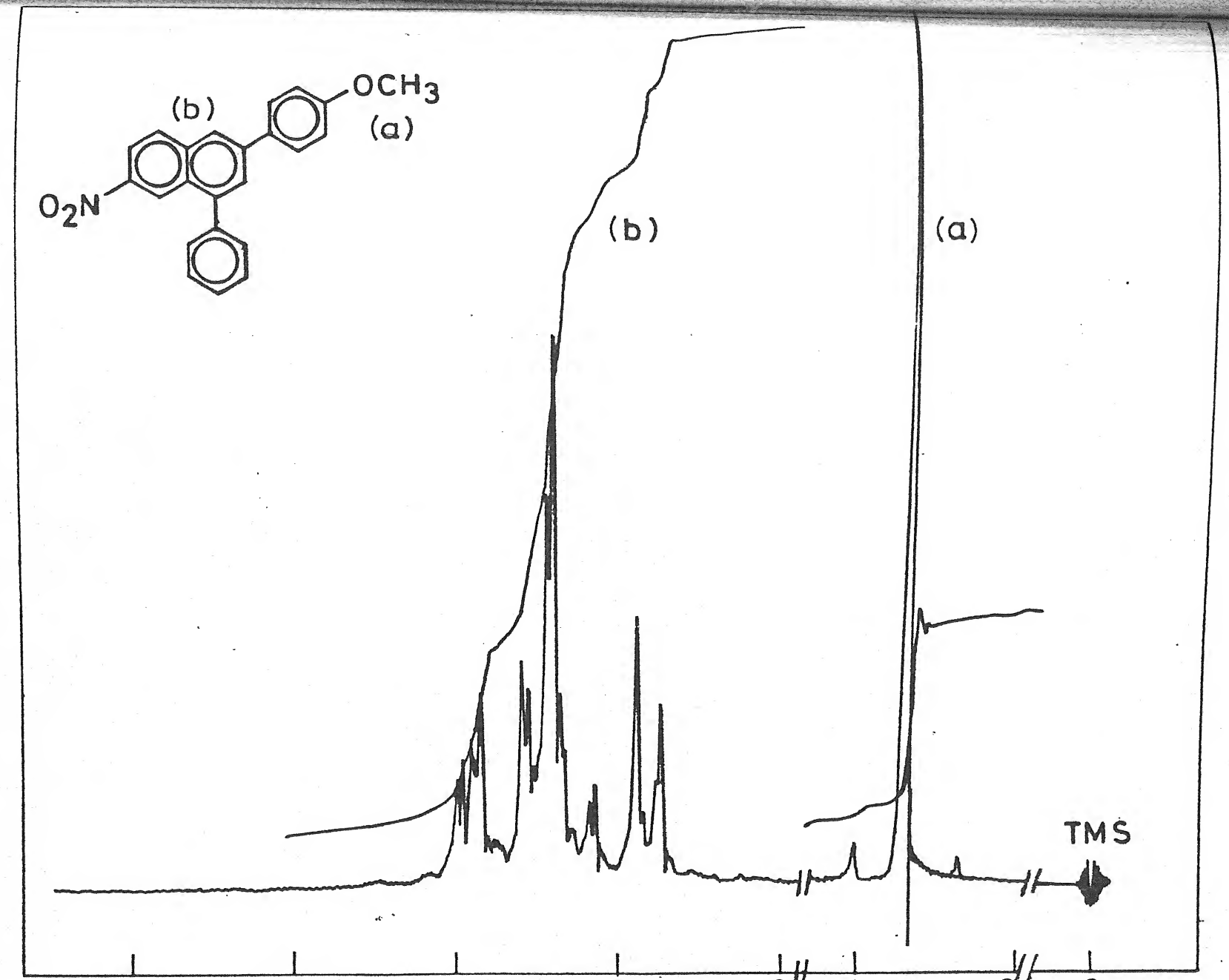
All the reagent were obtained from commercial sources i.e. BDH, S.Merck etc.. The starting materials were prepared according to references cited. Thus 4-nitrobenzyl



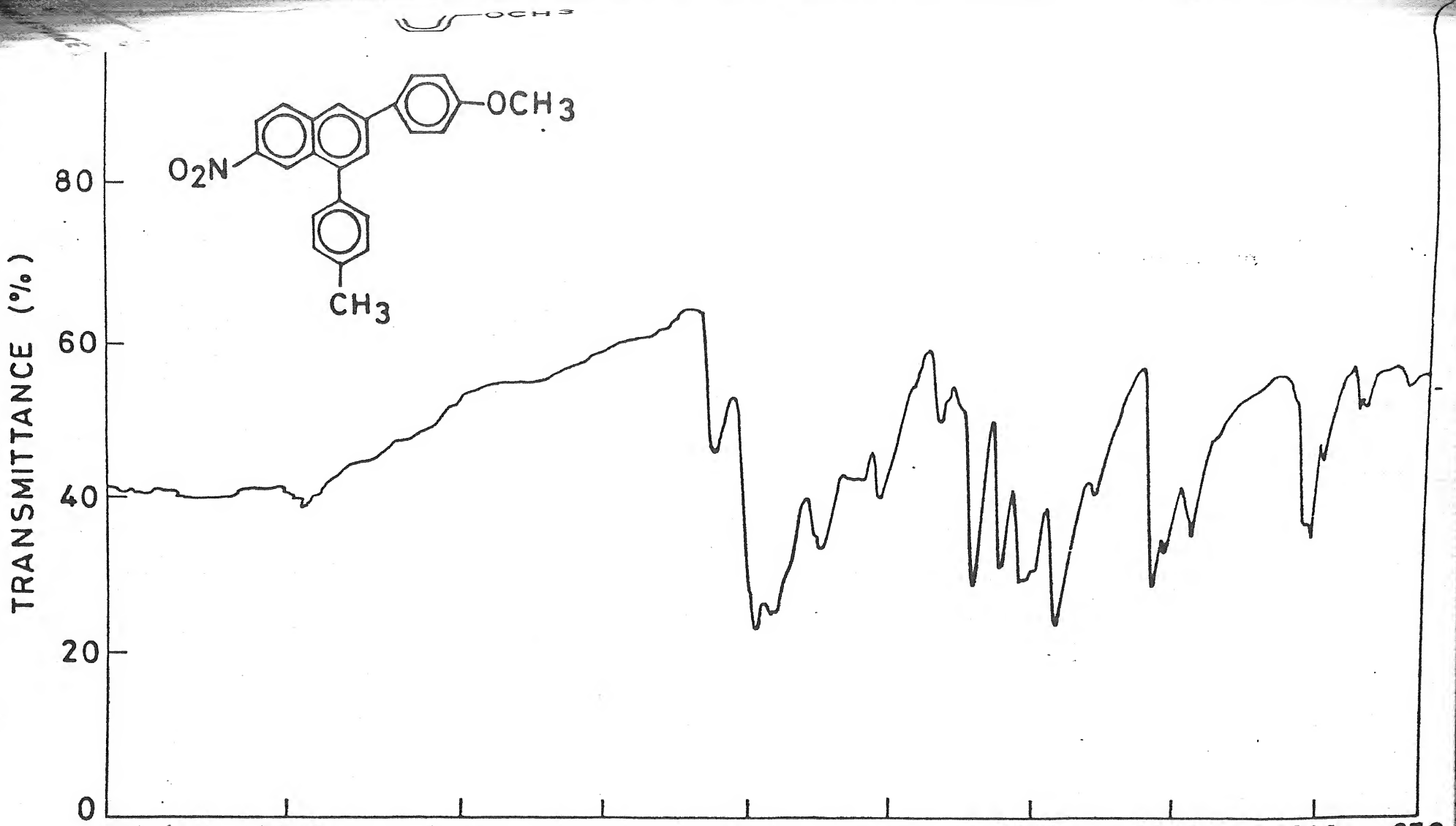
IR SPECTRUM OF COMPOUND (17 d)



NMR SPECTRUM OF COMPOUND (17f)



NMR SPECTRUM OF COMPOUND (18a)



IR SPECTRUM OF COMPOUND (18d)

bromide [18] was prepared by the direct bromination of 4-nitroluene at elevated temperature. Similarly benzyl bromide [19] was prepared from toulene.

The substituted benzylideneacetophenones, benzylidene 2-acetonaphthenes and benzylidene 2-acetothiophenes were prepared by a general procedure as citeed in Literature[6]. The methylketones react with equimolar quantities of aromatic aldehydes in presence of an alkali, with strring at 0 °C, to afford substituted benzylideneacetophenones . The resulting precipitate of α,β-unsaturated ketones was recrystallized from ethanol by benzene-petroleum ether (60-80°C) in 40-80 % yields.

V.4.2. Preparation of benzyltriphenylarsonium bromide (14 a)

A solution of triphenylarsine (50 mmole) and benzyl bromide (50 mmole) in 50 ml. of anhydrous benzene was allowed to reflux on a water bath for 4 hrs. A solid mass precipitated which was filtered, dried and recrystallized twice from chloroform and benzene to give white shining crystals of benzyltriphenylarsonium bromide in 76 % yield, m.p. 142-43°C (Lit. m.p.-141-42°C)[16].

V.4.3. Preparation of 4-nitrobenzyltriphenylarsonium bromide (14b)

A mixture containing 50 mmole of 4-nitrobenzyl bromide and 50 mmole of triphenylarsine in 50 ml. of anhydrous benzene, was heated on a water bath for 6-8 hrs. Excess of the solvent was evaporated and petroleum ether (60-80°C) was added to precipitate

4-nitrobenzyltriphenylarsonium bromide (14b). This salt (14b) was twice recrystallized from chloroform and petroleum ether (60-80 °C) to give a pale yellow crystalline compound, m.p. 150-52°C (Lit.m.p. 150-51 °C)[17], yield 70 %.

V.4.4. Preparation of 1,3-diarylnaphthalenes (17 a-j).

In a mixture of benzyltriphenylarsonium bromide (3 mmole)in glacial acetic acid (30 ml.) containig zinc chloride (1 g.) and sodium acetate (1 g.). a solution ofα,β-unsaturated ketone (3mmole) in glacial acetic acid (10 ml.)was added slowly with strring under nitrogen atmosphere. This reaction mixture was refluxed for 6-8 hrs., left overnight at room temperature and then diluted with cold water (30 ml.)to precipitate a solid mass of naphthalene derivatives. This solid mass was seperated by filtration and washed twice with methanol and subjected to column chromatography using neutral alumina as absorbent and benzene-petroleum ether (1:2) as eluent.The product thus obtained was recrystallized from a suitable solvent to give better yield of the desired products. (17a-j) (Scheme V.5). The suitable solvents for recrystallization are tabulated in Table V.1. The NMR spectral data, IR data are cited in Table V.2.

V.4.5. Preparation of 1,3-diaryl-7-naphthalenes (18 a- g)

In a 100 ml. round bottom flask, equipped with a reflux condensor and a magnetic stirrer, was placed a solution of 4-nitrobenzyltriphenylarsonium bromide (14b) (3 mmole) in 10 ml.

of glacial acetic acid followed by the addition of zinc chloride (1 g.) and 3 mmole of α,β-unsaturated ketone. The mixture was stirred at 200°C for 6-8 hrs. , under nitrogen atmosphere. The resulting solution was allowed to stand overnight at the room temperature. Ice cold water (30 ml.) was then added to precipitate a solid mass. The precipitated solid, so obtained, was filtered off, dried and chromatographed over netural alumina with chloroform fraction, which on recrystallization from an appropriate solvent gave a fine crystalline solid due to formation of 1,3-diaryl-7-nitronaphthalenes (14a-g).

All the naphthalenes derivatives (17a-j) and (18a-g) were prepared using the same general procedure . Their physical and spectral constants are listed in Table V.1. and Table V.2 respectively.

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Table v.1 Physical properties of 1,3-diarylnaphthalenes (17a-j) and 1,3-diaryl-7-nitronaphthalenes (18a-g)

Compd.	X	R^1	R^2	yield (%)	m.p. (°C)	recyt. solvt.	analysis found/ (calcd.)(%) C	H
1	2	3	4	5	6	7	8	9
17a	H	C_6H_5	C_6H_5	55	108-10 (109-10)[18]	A	94.3 (94.3)	5.8 (5.7)
b	H	4-$CH_3OC_6H_4$	C_6H_5	60	85-89	A	89.1 (89.0)	5.9 (5.8)
c	H	3,4-di-$CH_3OC_6H_3$	C_6H_5	52	59-60	A	84.7 (84.7)	5.8 (5.9)
d	H	3,4-$CH_2O_2C_6H_3$	C_6H_5	55	99-92	B	85.1 (85.2)	5.0 (4.9)
e	H	C_6H_5	4-$CH_3C_6H_4$	56	52-53	B	93.9 (93.9)	6.1 (6.1)
f	H	4-$CH_3OC_6H_4$	4-$CH_3C_6H_4$	54	118-20	B	89.0 (88.9)	6.2 (6.2)
g	H	4-ClC_6H_4	C_6H_5	70	85-86	A	83.9 (83.9)	4.8 (4.8)
h	H	4-$CH_3OC_6H_4$	4-ClC_6H_4	58	108-10	B	80.1 (80.1)	5.0 (4.9)

Table V.1 (Contd.)

1	2	3	4	5	6	7	8	9
17i	H	4-$(CH_3)_2NC_6H_4$	C_6H_5	45	76-77	B	89.2	6.6
							(89.2)	(6.5)
j	H	C_6H_5	4-ClC_6H_5	65	81-82	A	83.9	4.8
							(83.9)	(4.8)
18a	NO_2	4-$CH_3OC_6H_4$	C_6H_5	50	128-30	A	77.6	5.1
							(77.5)	(5.0)
b	NO_2	3,4-di-$CH_3OC_6H_3$	C_6H_5	45	131-33	A	74.5	5.2
							(74.6)	(5.2)
c	NO_2	3,4-di-$CH_2O_2C_6H_3$	C_6H_5	42	90-95	B	74.6	4.1
							(74.8)	(4.0)
d	NO_2	4-$CH_3OC_6H_4$	4-$CH_3C_6H_4$	50	75-78	B	78.0	5.1
							(78.1)	(5.2)
e	NO_2	4-$CH_3C_6H_4$	C_6H_5	55	123-25	A	81.5	5.1
							(81.4)	(5.0)
f	NO_2	4-$CH_3OC_6H_4$	4-ClC_6H_4	50	128-30	A	70.9	4.1
							(70.9)	(4.1)
g	NO_2	4-$CH_3C_6H_4$	4-$CH_3OC_6H_4$	52	114-16	A	78.0	5.1
							(78.1)	(5.2)

A = benzene-petroleum ether ;

B = chloroform-petroleum ether.

Table V 2 Spectral data of 1,3-diarylnaphthalenes (17a-j) and 1,3-diaryl-7-nitronaphthalenes (18a-g).

Comd.	IR data (KBr) cm^{-1}		NMR($CDCl_3$) data		
	$\nu C=C$	$\phi C-H$	δ(ppm)	No.of protons	Assignment
1	2	3	4	5	6
17a	1595	996	-	-	-
b	1605	998	6.50-8.10,m	15 H	Ar-H
			3.78,s	3 H	OCH_3
c	1599	989	6.70-8.25,m	14 H	Ar-H
			3.75,d,J=5Hz	6 H	2xOCH_3
d	1600	990	6.60-8.10,m	14 H	Ar-H
			5.95,s	2 H	O_2CH_2
e	1605	997	6.68-8.15,m	15 H	Ar-H
			2.45,s	3 H	CH_3
f	1608	998	6.50-8.40,m	14 H	Ar-H
			3.75,s	3 H	OCH_3
			2.38,s	3 H	CH_3
g	1615	985	-	-	-
h	1603	998	6.50-8.15,m	14 H	Ar-H
			3.75,s	3 H	OCH_3

Table V.2 (contd.)

1	2	3	4	5	6
17 i	1598	996	6.69-8.30,m	14 H	Ar-H
			3.00,s	6 H	$-N(CH_3)_2$
j	1588	988	-	-	-
18 a	1592	990	6.85-8.28,m	14 H	Ar-H
			3.85,s	3 H	OCH_3
b	1698	992	-	-	-
c	1590	986	6.75-8.15,m	13 H	Ar-H
			6.05,s	2 H	O_2CH_2
d	1600	995	6.80-8.20,m	13 H	Ar-H
			2.35,s	3 H	CH_3
			3.78,s	3 H	OCH_3
e	1608	991	6.75-8.05,m	14 H	Ar-H
			2.38,s	3 H	CH_3
f	1612	994	6.88-8.16,m	13 H	Ar-H
			3.80,s	3 H	OCH_3
g	1610	996	6.80-8.20,m	13 H	Ar-H
			3.78,s	3 H	OCH_3
			2.35,s	3 H	CH_3

s = singlet ; m= multiplet ; d = doublet ;
ν = Stretching vibrations ; φ = out of plane deformation of hydrogen attached to aromatic nucleus.

CHAPTER VI

REACTIONS OF p-SUBSTITUTED PHENACYLIDENEAZOMETHINE INTERMEDIATES WITH WIDE RANGE OF AROMATIC ALDEHYDES : SYNTHESIS OF 2,4-DIARYL-6-(p-SUBSTITUTED PHENYL) PYRIMIDINES.

VI. 1 ABSTRACT

Some p-substituted phenacylpyridinium bromides have been prepared by the quaternization of pyridine with p-substituted phenacyl bromide in benzene at reflux temperature in fair to good yields. The aqueous solution of these pyridinium salts on treatment with K_2CO_3 yielded corresponding p-substituted phenacylideneazomethine intermediates. The reaction of these ylids with various aromatic aldehydes having electron attracting and repelling effect, was carried out in presence of ammonium acetate and glacial acetic acid at reflux temperature for 4 hrs. under nitrogen atmosphere, to give 2,4-diaryl-6-(p-substituted phenyl) pyrimidines in 40-60 % yield. Aammonium acetate in acetic acid was used as aza cyclization agent. The structuresof pyrimidines were confirmed on basis of elemental and spectral analysis.

VI.2 INTRODUCTION

Azomethine intermediates have gained considerable importance in the synthetic organic chemistry. They have used as

potential reagent in synthesis of pyridines,[1-2] indoles[3],tetrazines[4], cinnoleneS[5], naphthaleneS[6], azaridines[7] and several other heterocycles. Krohnke[8] first reported only a single reaction which involved the condensation of phenacylpyridinium bromide with 4-nitrobenzaldehyde to give 2,4 -di (4-nitrophenyl)-6-phenylpyrimidine. The detailed experimental conditions were not incorporated in the aforesaid reference. This reaction leading to synthesis of pyrimidine nucleus could not be duplicated until recently. Therefore, it seems to be pertinent to study the reaction of phenacypyridinium salts with a wide variety of aldehydes having electron attracting and donating effect.

In the present chapter some p-substituted phenacylpyridinium bromides are copuled with aromatic aldehydes in presence of mixture of ammonium acetate and glacial acetic acid with a view to confirm the course of the reactions.

VI.3 RESULTS AND DISCUSSION

Quaternisation of pyridine with phenacyl bromide,p-chlorophenacyl bromide, p-bromophenacyl bromide, p-methylphenacyl bromide, p-methoxyphenacyl bromide in benzene at reflux temperature, gave phenacylpyridinium bromide (1a), p-chlorophenacylpyridinium bromide (1b), p-bromophenacylpyridinium bromide (1c), p-methylphenacylpridinium bromide (1d) and p-methoxyphenacylpyridinium bromide (1e) respectively. The structures of pyridinium salts (1a-e) were confirmed by comparision of melting points of salts with those reported in the

literature and spectra data. The IR spectra of salts (1 a-e) showed a characteristic absorption band due to C — O stretching vibrations in the region 1700-1680 Cm^{-1} for carbonyl group. The dragnostic absorption bands in the region 3300-3000 Cm^{-1} were observed due to C-H stretching vibration of methylene group attached to nitrogen atom.

The treatment of these salts (1 a-e) with aqueous sodium carbonate gave corresponding azomethine intermediates (2a-e) which could not be stored due to sensitivity towards atmospheric components and lack of stabilizing factors . Hence they could not be used in subsequent reactions . The reaction was, therefore carried out by generating the ylid intermediates (2a-e) 'in situ' from the corresponding salts (1 a-e).

Heating the mixture of pyridinium salts (1a-e) with substituted benzaldehyde (2 a-c) in presence of ammonium acetate and glacial acetic acid at reflux temperature gave 2,4-di (substituted phenyl)-6- substituted phenylpyrimidine (5 a-o) in 40-80 % yields (Scheme VI.1).

Further attempts were made to synthesize symmetrical pyrimidines having identical substituents at 2,4,6 positions. Thus p-chlorophenacylpyridinium bromide (1b) with p-chlorobenzaldehyde (6a), p-bromophenacylpyridinium bromide (1c) with p-bromobenzaldehyde (6b), p-methylphenacylpyridinium bromide (1d) with tolualdehyde (6c) and p-methoxyphenacyl pyridinium bromide (1e) with anisaldehyde (6d) were heated in a mixture of ammonium acetate and glacial acetic acid to give

2,4,6-tri(p-chlorophenyl)pyrimidine (7a),2,4,6-tri(p-bromophenyl) pyrimidine (7b), 2,4,6-tri (p-tolys)pyrimidine (7c) and 2,4,6-tri (p-methoxylphenyl) pyrimidine (7d) respectively in good yields (Scheme VI.2).

The course of reaction is similar to Mannich type of reaction. The methylene groups of salts (1) and aromatic aldehyde (2) in presence of liquid ammonia, react to form Mannich base-a pyridinium salt (3) which than further undergoes condensation with another molecule of aldehyde in NH_3 to form azomethine intermediate (4). This undergoes elimination of pyridine hydroamide and H_2 to form 2,4,6-triarylpyrimidines [(5a-b)&(7a-d)].

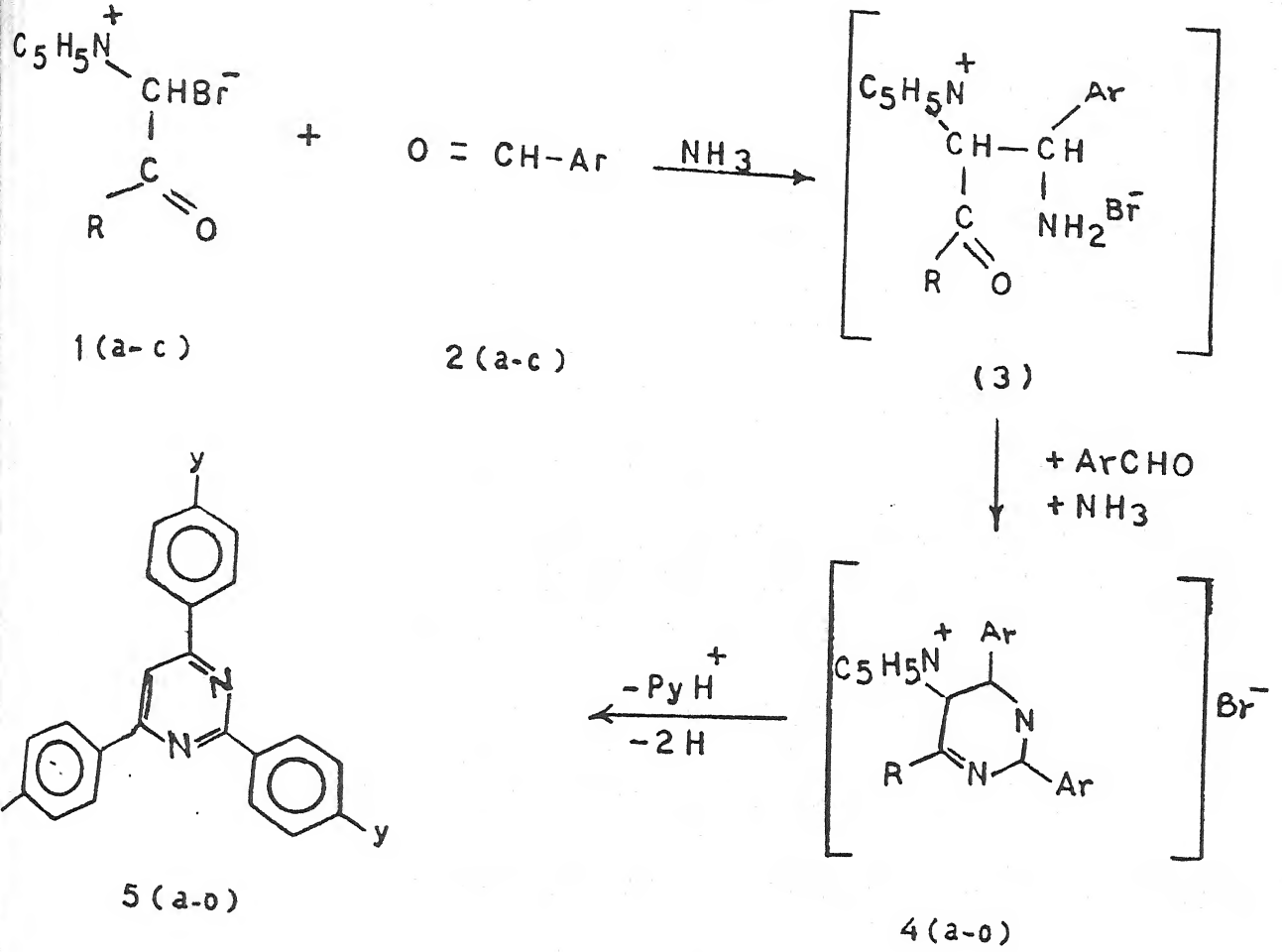
Various new 2,4,6-triarylpyrimidines [(5a-o) &(7a-d)] synthesized by above route are listed in Table VI.1. All the pyrimidines gave satisfactory elemental and spectral analysis. The IR spectral data showed a characteristic absorption bands in the region 3100-3000 Cm^{-1}, which were assigned to the C-H stretching mode of pyrimidine rings. Two bands in the region 1600 and 1500 Cm^{-1} were due to interaction between C=C and C=N vibrations of the ring. The NMR spectra of pyrimidines showed a pyrimidyl proton (C_5—H) in the range δ6.60-6.80 and aromatic proton in the region δ6.60-8.40.

VI.4. EXPERIMENTAL

VI.4.1 Starting Materials

All the reagents were obtained from commercial sources

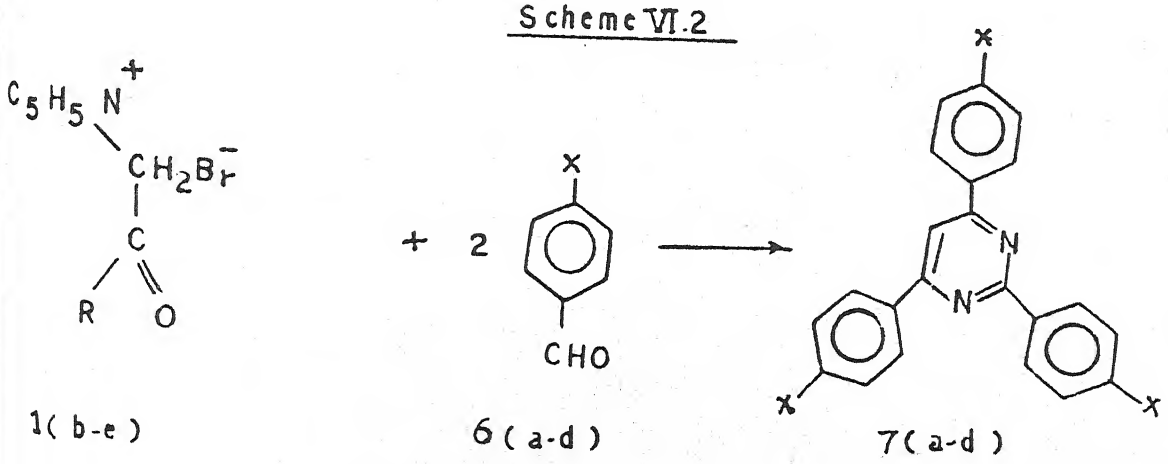
Scheme VI.1



1(a-c) 2(a-c) (3)

5(a-o) 4(a-o)

Scheme VI.2



1(b-e) 6(a-d) 7(a-d)

(E.Merck, BDH, SISCO etc). Starting materials were prepared according to the procedure reported in Literature.

VI.4.2 Preparation of p-substituted phenacylpyridinium bromide (1 a-e)

General Procedure

A solution of 100 mmole. of p-substitutedphenacyl bromide and 100 mmole of pyridine in 100 ml of anhydrous benzene or tetrahydrafuran, was boiled for 6-8 hrs. The excess of the solvent was evaporated and petroleum ether was added to precipitate the salts (1a-e) which were, then recrystallized from chloroform, Petroleum ether (1:2). This procedure was followed to prepare the following salts.

(i) Phenacylpyridinium bromide (1a), Pale yellow crystals m.p:192-93°C (Lit m.p.-195-97°C)[9] ; IR (KBr) 1690 Cm^{-1} (νC=O).

(ii) 4-chlorophenacylpyridinium bromide (1b), White crystals, m.p.- 208-10°C (Lit. m.p:207°C)[10] ; IR (KBr) 1680 Cm^{-1} (νC=O).

(iii) 4-Bromophenacylpyridinium bromide (1c),White crystals, m.p.- 240-42°C (Lit. m.p:242-43°C)[9] ; IR (KBr)1680 Cm^{-1} (νC=O).

(iv)4-Methylphenacylpyridinium bromide (1d), light reddish chite crystals,m.p:201-03°C (Lit.m.p.- 205°C)[8] ; IR (KBr) 1680 Cm^{-1} (νC=O).

(v) 4-Methoxyphenacylpyridinium bromide (1 e) white crystals,m.p. 206-08°C (Lit.m.p.-209-10°C)[9] ;IR (KBr) 1678 cm^{-1} (νC=O).

VII.4.3 Preparation of 2,4,6-triarylpyrimidines [(5a-o)&(7a-o)]

General procedure

A mixture of 3 mmole of substitutedphenacylpyridinium bromide (1a-e) and 6 mmole of aromatic aldehydes (2a-c) & (6a-d) in 50 ml. of glacial acetic acid was stirred at the room temperature for 6-8 hrs.. This mixture was refluxed for 4-6 hrs. and left, overnight at room temperature. The mixture was then poured into ice cold water (50 ml.), which was constantly stirred. Thus solid mass was precipitated. This precipitate was filtered, washed twice with water and methanol and dried.On crystallization with approprite solvent, the precipitate gave crystalline product, titled pyrimidines (50 a-o) & (7 a-d) in 40-80 % yields as depicted in Table (VI.1).

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Table VI .1. Physical Properties Of 2,4-di (substituted phenyl) -6 - substituted phenyl pyrimidines (5 a-o) and 2,4,6 -tri substituted phenyl pyrimidines (7 a-d).

Compd.	X	Y	yield (%)	recryst. solvent	m.p. (C)	analysis found/(calc.)(%) C	H	N
1	2	3	4	5	6	7	8	9
5a	4-H	4-H	50	A	70-72	85.74	5.12	9.12
						(85.71)	(5.19)	(9.09)
b	4-H	4-NO_2	80	A	105-07	66.28	3.49	14.05
						(66.33)	(3.51)	(14.07)
c	4-H	4-$N(CH_3)_2$	45	B	60-62	79.14	6.52	14.18
						(79.18)	(6.59)	(14.21)
d	4-Cl	4-H	50	B	115-17	77.03	4.32	8.14
						(77.08)	(4.37)	(8.17)
e	4-Cl	4-NO_2	60	C	120-22	61.08	3.05	12.99
						(61.04)	(3.00)	(12.94)
f	4-Cl	4-$N(CH_3)_2$	48	B	144-46	74.85	6.04	13.40
						(74.90)	(6.00)	(13.44)
g	4-Br	4-H	60	A	132-34	68.17	3.82	7.18
						(68.21)	(3.87)	(7.23)
h	4-Br	4-NO_2	65	B	110-12	55.28	2.67	11.69
						(55.34)	(2.72)	(11.74)

Table. VI.I (Contd.)

1	2	3	4	5	6	7	8	9
5i	4-Br	3,4-OCH_3	48	A	70-71	61.48	4.48	5.47
						(61.53)	(4.53)	(5.52)
j	4-CH_3	4-H	50	B	84-86	85.76	5.53	8.63
						(85.71)	(5.59)	(8.69)
k	4-CH_3	4-NO_2	60	A	98-100	66.93	3.85	13.52
						(66.99)	(3.88)	(13.59)
l	4-CH_3	4-$N(CH_3)_2$	55	C	61-63	79.37	6.79	13.67
						(79.41)	(6.86)	(13.72)
m	4-OCH_3	4-NO_2	65	B	78-80	64.42	3.69	13.02
						(64.48)	(3.73)	(13.08)
n	4-OCH_3	4-$N(CH_3)_2$	66	C	58-59	76.38	6.54	13.14
						(76.41)	(6.60)	(13.20)
o	4-OCH_3	4-H	50	C	68-70	81.61	5.28	8.21
						(81.65)	(5.32)	(8.28)
7a	4-Cl	4-Cl	48	A	120-22	64.14	3.13	6.77
						(64.11)	(3.16)	(6.80)
b	4-Br	4-Br	63	B	108-10	48.51	2.31	5.05
						(48.44)	(2.39)	(5.14)
c	4-CH_3	4-CH_3	54	B	90-92	85.64	6.63	8.09
						(85.71)	(6.29)	(8.00)
d	4-OCH_3	4-OCH_3	61	C	98-100	75.47	7.12	5.46
						(75.38)	(7.04)	(5.53)

A= chloroform ; B= Pet. ether ; C= Methanol

Table VI.2 IR spectra data of 2,4-di(substituted phenyl)-6-(substituted phenyl)pyrimidine (5a-o) and 2,4,6-tri(substituted phenyl) pyrimidines (7a-d)

Compd.	ν C-H	ν C=C	ν C=N	φ C-H	ν C-NO_2	ν C-X (X=Cl or Br)
5a	3095	1595	1515	995	–	–
b	3090	1600	1510	1000	1560,1340	–
c	3100	1605	1505	990	–	–
d	1105	1600	1515	995	–	750
e	3100	1608	1510	996	1565,1340	760
f	3120	1615	1518	955	–	768
g	3060	1590	1510	990	–	610
h	3065	1598	1500	1000	1560,1330	605
i	3070	1610	1510	1005	–	620
j	3080	1615	1520	1000	–	–
k	3110	1605	1510	1005	1575,1340	–
l	3060	1595	1505	995	–	–
m	3095	1595	1505	1010	1580,1335	–
n	3090	1600	1500	1000	–	–
o	3105	1610	1505	1010	–	–
7a	3095	1600	1510	995	–	760
b	3085	1605	1508	998	–	605
c	3095	1602	1512	989	–	–
d	3090	1610	1515	992	–	–

ν = stretching vibrations ; φ = out of plane deformation of hydrogens attached to aromatic nucleus.

Table VI.3 NMR data of 2,4-di(substituted phenyl)-6-(substituted phenyl) pyrimidines (5a-o) and 2,4,6-tri(substituted phenyl)pyrimidines

Compd.	δ(ppm)	no.of protons	assignment
1	2	3	4
5a	6.65-7.80,m	15 H	Ar-H
	6.50,s	1 H	PyH(C_5-H)
b	6.80-7.85,m	13 H	Ar-H
	6.60,s	1 H	PyH(C_5-H)
c	6.70-7.75,m	13 H	Ar-H
	6.60,s	1 H	PyH(C_5-H)
	2.97,s	12 H	di-N(CH_3)$_2$
d	6.78-7.88,m	14 H	Ar-H
	6.60,s	1 H	PyH(C_5-H)
e	6.95-8.15,m	12 H	Ar-H
	6.78,s	1 H	PyH(C_5-H)
f	6.85-7.88,m	12 H	Ar-H
	6.75,s	1 H	PyH(C_5-H)
	2.95,s	12 H	di-N(CH_3)$_2$
g	6.85-8.15,m	14 H	Ar-H
	6.70,s	1 H	PyH(C_5-H)
h	7.00-8.02,m	12 H	Ar-H
	6.78,s	1 H	PyH(C_5-H)

Table VI.3 (Contd.)

1	2	3	4
5 i	6.89-8.15,m	10 H	Ar-H
	6.70,s	1 H	PyH(C_5-H)
	3.85,d(J=6H_z)	12 H	di(3,4-diOCH_3)
j	6.85-8.05,m	14 H	Ar-H
	6.65,s	1 H	PyH(C_5-H)
	2.45,s	3 H	CH_3
k	6.85-8.15,m	12 H	Ar-H
	6.75,s	1 H	PyH(C_5-H)
	2.55,s	3 H	CH_3
l	6.78-7.85,m	12 H	Ar-H
	6.68,s	1 H	PyH(C_5-H)
	2.38,s	3 H	CH_3
	3.05,s	12 H	di-N(CH_3)$_2$
m	6.75-8.25,m	12 H	Ar-H
	6.68,s	1 H	PyH(C_5-H)
	3.85,s	3 H	OCH_3
n	6.85-8.25,m	12 H	Ar-H
	6.65,s	1 H	PyH(C_5-H)
	3.75,s	3 H	CH_3
	2.97,s	12 H	di-N(CH_3)$_2$

Table VI.3 (Contd.)

1	2	3	4
5 o	6.85-7.95,m	14 H	Ar-H
	6.70,s	1 H	PyH(C_5-H)
	3.75,s	3 H	OCH_3
7 a	6.80-7.90,m	12 H	Ar-H
	6.62,s	1 H	PyH(C_5-H)
b	6.75-7.85,m	12 H	Ar-H
	6.55,s	1 H	PyH(C_5-H)
c	6.88-7.98,m	12 H	Ar-H
	6.68,s	1 H	PyH(C_5-H)
	2.55,s	9 H	tri-CH_3
d	6.90-8.10,m	12 H	Ar-H
	6.65,s	1 H	PyH(C_5-H)
	3.80,s	9 H	tri-OCH_3

s = singlet

m = multiplet

d= doublet

CHAPTER VII

REACTIONS OF BENZYLPYRIDINIUM BROMIDE AND O - CHLOROBENZYL PYRIDINIUM BROMIDE WITH α,β-UNSATURATED KETONES : SYNTHESIS OF SOME NEW 1,3 -DISUBSTITUTED NAPHTHALENES AND 1,3,5-TRISUBSTITUTED NAPHTHALENES*

VII.1 ABSTRACT

The pyridinium salts and their ylid intermediates have been utilized in the synthesis of a wide variety of heterocyclic compounds[1-12]. But little attention has been paid towards the synthesis of carbocyclic systems especially leading to the naphthalene nucleus by the interaction of azomethine intermideates and α,β—unsaturated ketones.[13]. With a view to explore the domain of such a reaction, we have studied the reactions of substituted benzylpyridinium salts with different α,β-unsaturated ketones, in the presence of anhydrous aluminium chloride or zinc chloride in a mixture of sodium acetate in glacial acetic acid as cyclization agent.

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* Part of this worked is published in Current Science,54,571-574 (1985)

The experimental techniques were the same as reported eariler.[2-4]. Both the pyridinium salts were prepared by heating benzylbromide and o-chlorobenzylbromide with pyridine in dry benzene.[14,15] . The strucure of products were estabilished by IR and NMR spectral data.

VII.2 INTRODUCTION

From the literature survey it was clear that various methods were investigated for the synthesis of naphthalenes derivatives. Several steps were involved in synthesis of naphthalene derivatives which affect the yield of the final products. For synthesis of naphthalene derivatives, House et al.[16,17] made the frist attempt. They synthesized 1,8-diphenylnaphthalene (3) by the reaction of 8-phenyl-Δ1,10-octal-1-one (1) with phenylmagnesium bromide to form an alcohol (2), which underwent dehydrogenation and dehydration with 2,3-dichloro-5-,6-dicyanobenzoquinone in boiling benzene to afford the desired product(3) (Scheme VII.1). Since this route involved several steps to form the final product, the yield was poor.

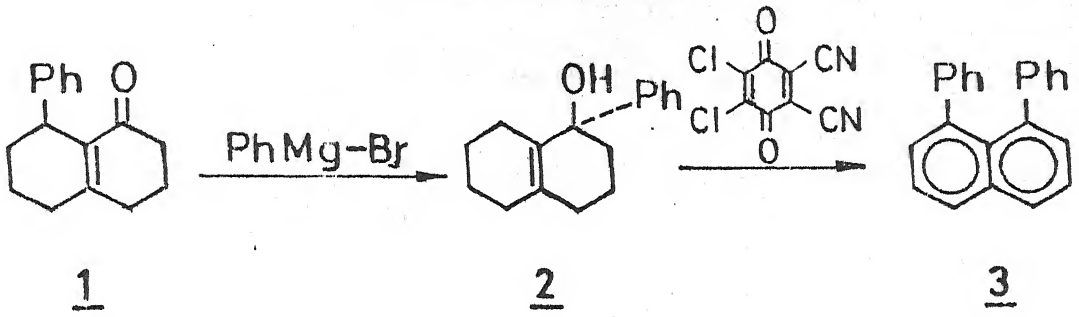
Many years after House et al., another route for the synthesis of naphthalene derivatives has been investigated.[18] In this new investigation the new naphthalene derivatives named 1,8-diphenylnaphthalene (9) was synthesized. The synthesis of 1,8-diphenylnaphthalene involves several steps. According to this synthesis , first reduction of 1,4,5,8,9,10- hexahydro-1,4-dioxo-5-phenylnaphthalene (4) took place. Then the resulting product

forms thioketal (6) with ethanolithioldesulfurisation with raney nickel and resulting product then treated with phenyllithium to give 1-(trans)-hydroxy-cis-syn-1,8-diphenyldecaline (8). On dehydrogenation with Pd/C (30%),1- (trans)-hydroxy-cis-syn-1,8-diphenyldecaline gave desired product (9) (Scheme VII.2).

After some years a convinient and facile route was reported by Krohnke et al.[16] and Tewari et al.[17]. From this synthesis 1,3-diphenylnaphthalene (12) was synthesized by the interaction of benzylpyridinium bromide (10) on benzalacetophenone (11) in presence of anhydrous zinc chloride as cyclization agent (Scheme VII.3). This method proved better than aforementioned methods, because it involves only single step and gave quantitative yield of the desired product. Furthermore, this reaction allows selective introduction of substituents at 1 and 5 positions of the naphthalene nucleus. However, only a few reactions, adopting this procedure have been reported but detailed experimental condsitions have not been described.Prompted from this work it seemed to be of great interest to explore the domain of applicability of this new route.

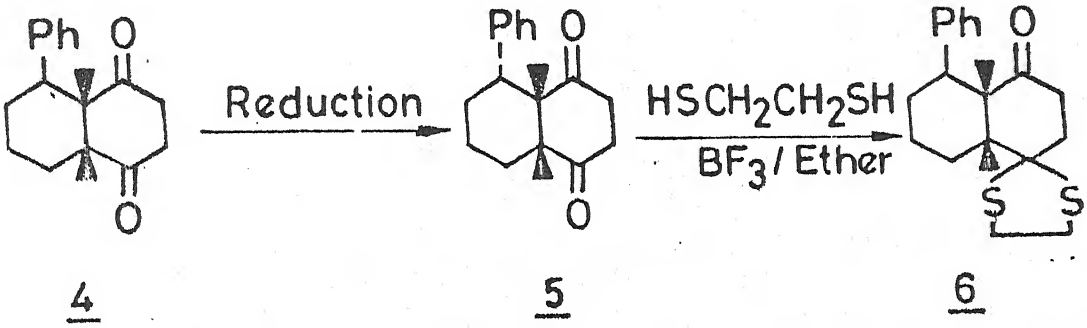
In the present chapter, we have reported the reaction of benzylpyridinium bromide and o-chlorobenzylpyridinium bromide with various substituted benzylideneacetophenones with a view to investigate the applicability of this route in the sythesis of a wide range of naphthalene derivatives.

Scheme VII · 1

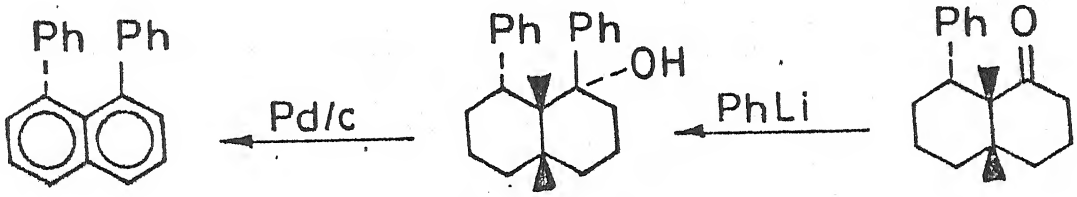


1 2 3

Scheme VII · 2

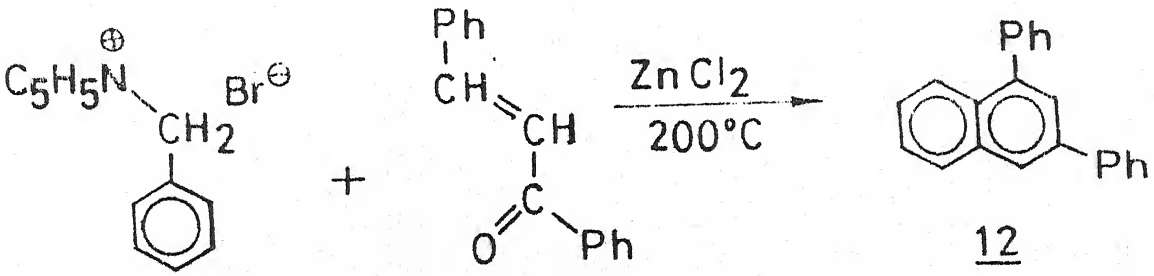


4 5 6



9 8 7

Scheme VII · 3



10 11 12

VII.3 RESULTS AND DISCUSSION

Reaction of benzyl bromide (13a) and o-chlorobenzyl bromide (13b) with pyridine in benzene at reflux temperature gave benzylpyridinium bromide (14a) and o-chlorobenzylpyridinium bromide (14b) (Scheme VII.4).

The stuctures of benzylpyridinium bromide (14a) and o-chlorobenzylpyridinium bromide (14b) were confirmed on the basis of IR and NMR spectral data . The IR spectra of 14a and 14b showed a diagnostic absorption band of strong intensity at 3045 and 3050 cm. $^{-1}$ respectively due to C-H stretching vibration band of methylene group attached to a position adjacent to nitrogen atom . Characteristic absorption bands due to - Cl group in salt (14b) were obtained at 790 cm.$^{-1}$. The NMR spectrum of salts (14a-b) showed a singlet at δ6.30 and δ6.35 due to the methylene protons and aromatic protons appeared in the range δ6.80-9.50.

The reactions of these salts (14a-b) were carried out with a wide range ofα,β-unsaturated carbonyl compounds in the presence of anhydrous $AlCl_3$ and $ZnCl_2$ in a mixture of sodium acetate and acetic acid at 200 $^{\circ}$C to afford 1,3-diarylnaphthalenes and 1,3-diaryl-5-chloronaphthalenes in 50-75% yields. It was however observed that the yields of resulting naphthalenes were dependent upon the nature of substituents attached to the pyridinium salts as well as to the α,β-unsaturated ketones. The reactivity of salt (14b) was lower than the (14a) because of - I effect of Cl group which stabilized the carbanion formation . Hence salt (14b) afforded lower yield of naphthalene derivatives

than salt (14a).

The reaction seems to proceed via the intermediacy of a betaine type of derivative (16), which is formed by the nucleophilic attack of the ylid carbons (15a-b) presumably generated ' in situ ' by dehydrogenation of the salts (14a-b), on the β — carbon of α,β-unsaturated ketone. Betaine (16), then undergoes cyclization in presence of anhydrous $ZnCl_2$ and $AlCl_3$ used as cyclization agents to afford naphthalene derivatives (17a-i & 18a-m). (Scheme VII.5)

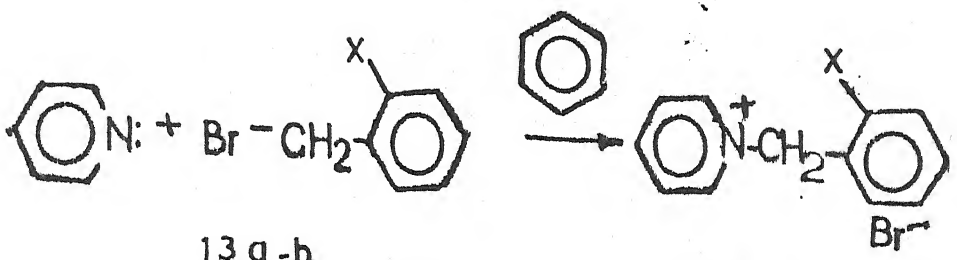
All naphthalenes (17a-18m) obtained in the present investigations were crystalline solids usually soluble in chloroform, pyridine and acetone. All physical and spectral data have been repoted in Table VII.1. All the compounds are new and gave satisfactory elemental analysis . The IR spectra of naphthalene derivatives showed a double absorption maxima in the region 1612-1590 cm^{-1} which were assigned to the stretching vibrations of carbon-carbon double bond. The strong bands in region 900-850 cm^{-1} were diagnostic of absorption of polynuclear aromatics . The chloro group of the products showed a strong asymmetrical stretching band at 730-805. The NMR spectra of compounds, in general, exhibited aromatic multiplet in range δ6.50-8.50.

VII.4 EXPERIMENTAL

VII.4.1 Starting Materials

All the reagents were obtained from commercial sources

Scheme VII 4



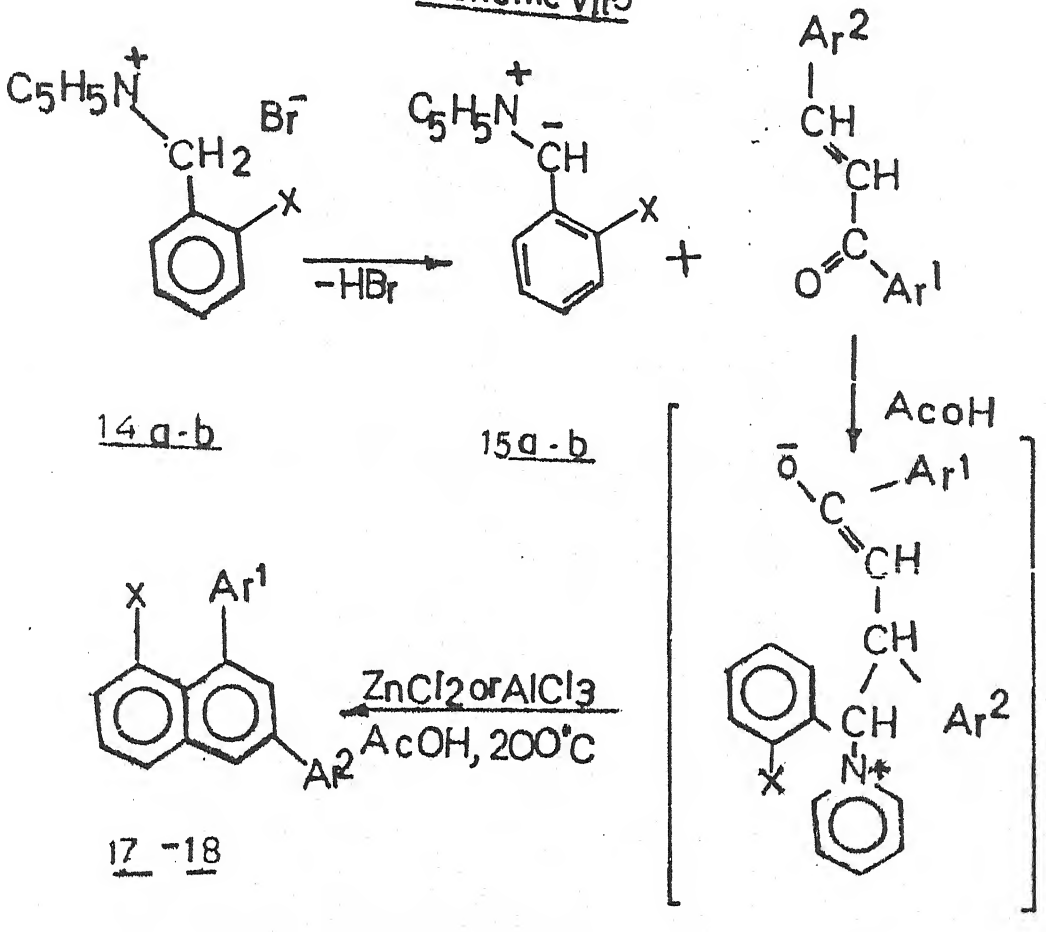
13 a-b

13 & 14a , X=H

13 & 14b, X=Cl

14 a-b

Scheme VII-5



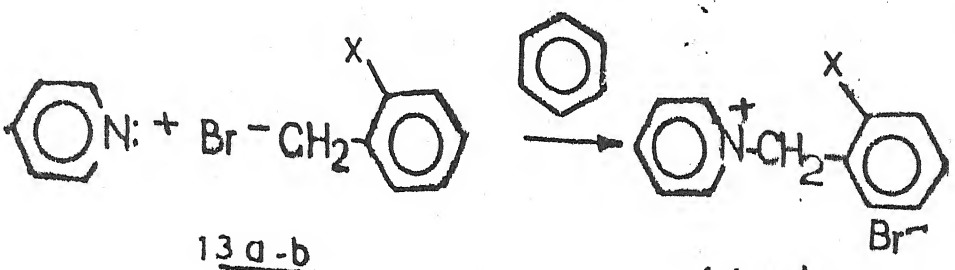
14 a-b

15 a-b

16

17 -18

Scheme VII 4



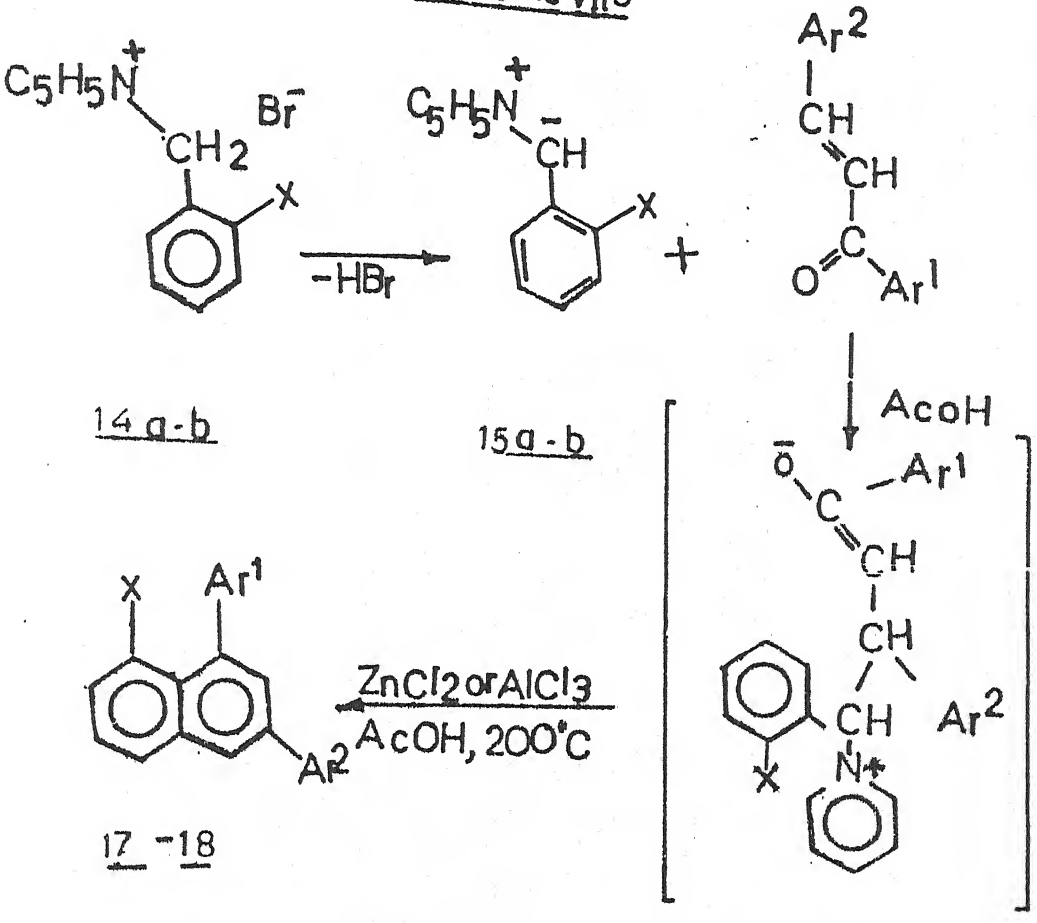
13 a-b

13 & 14a , X=H

13 & 14b, X=Cl

14 a-b

Scheme VII 5

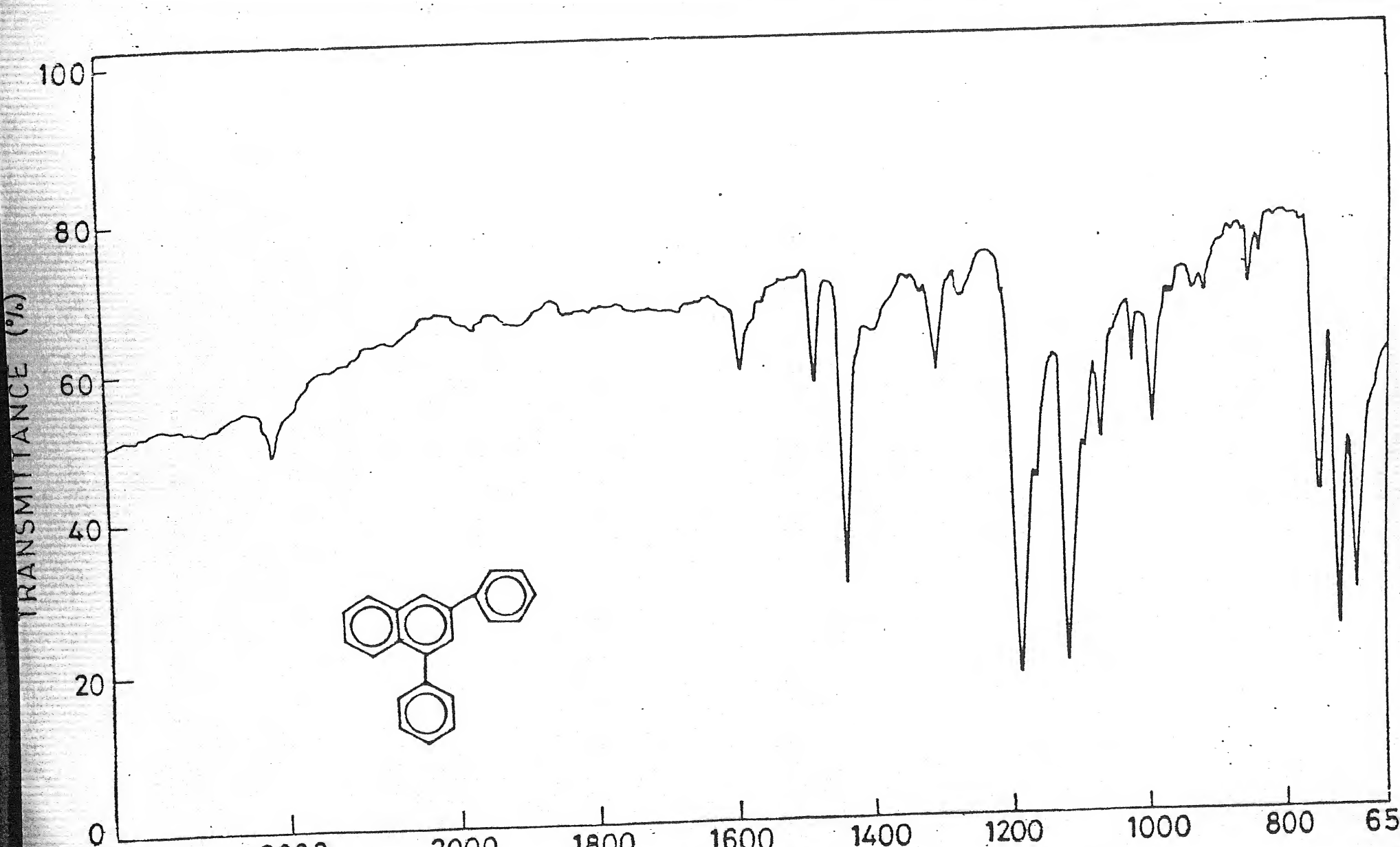


14 a-b

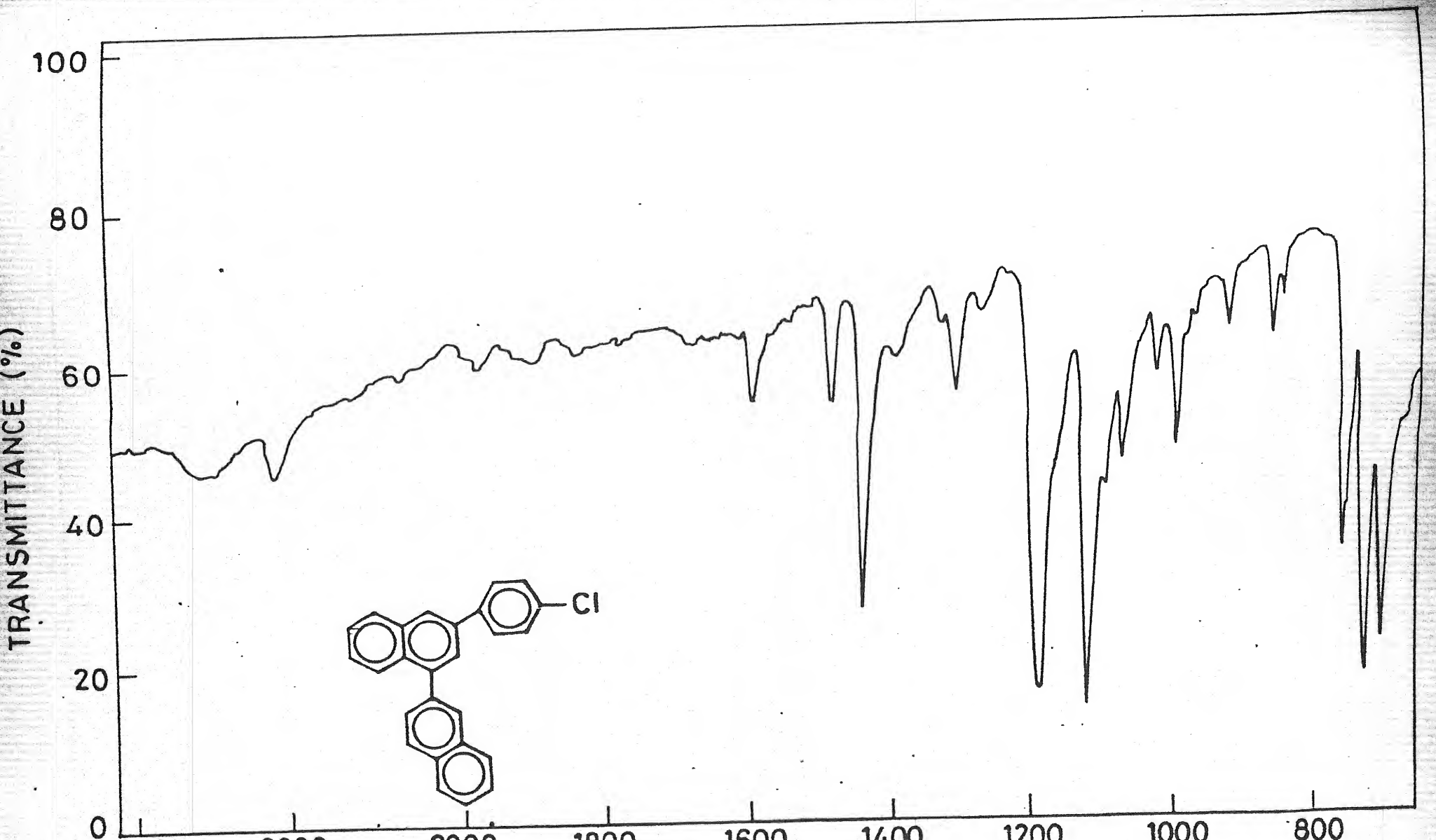
15 a-b

16

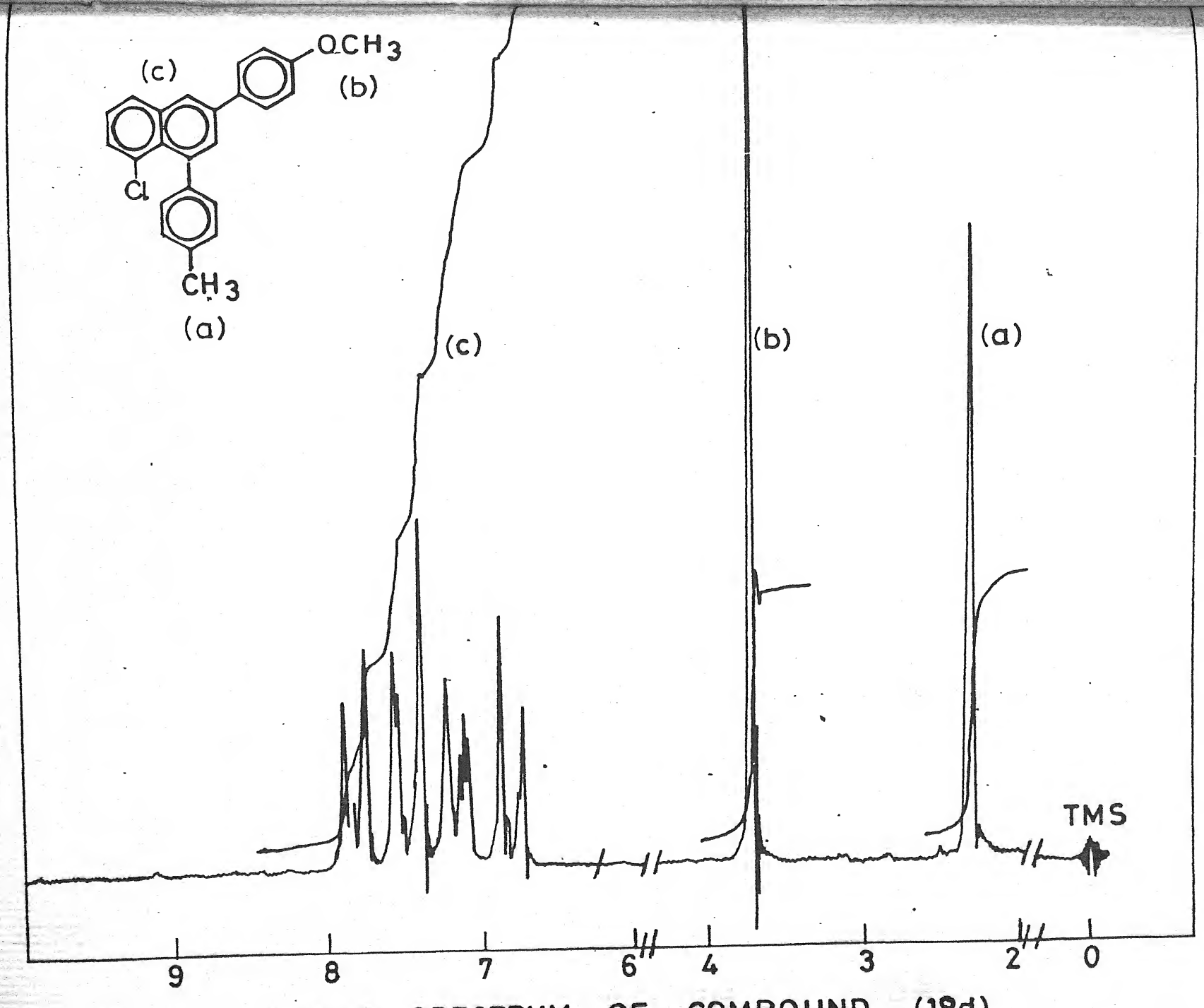
17 -18



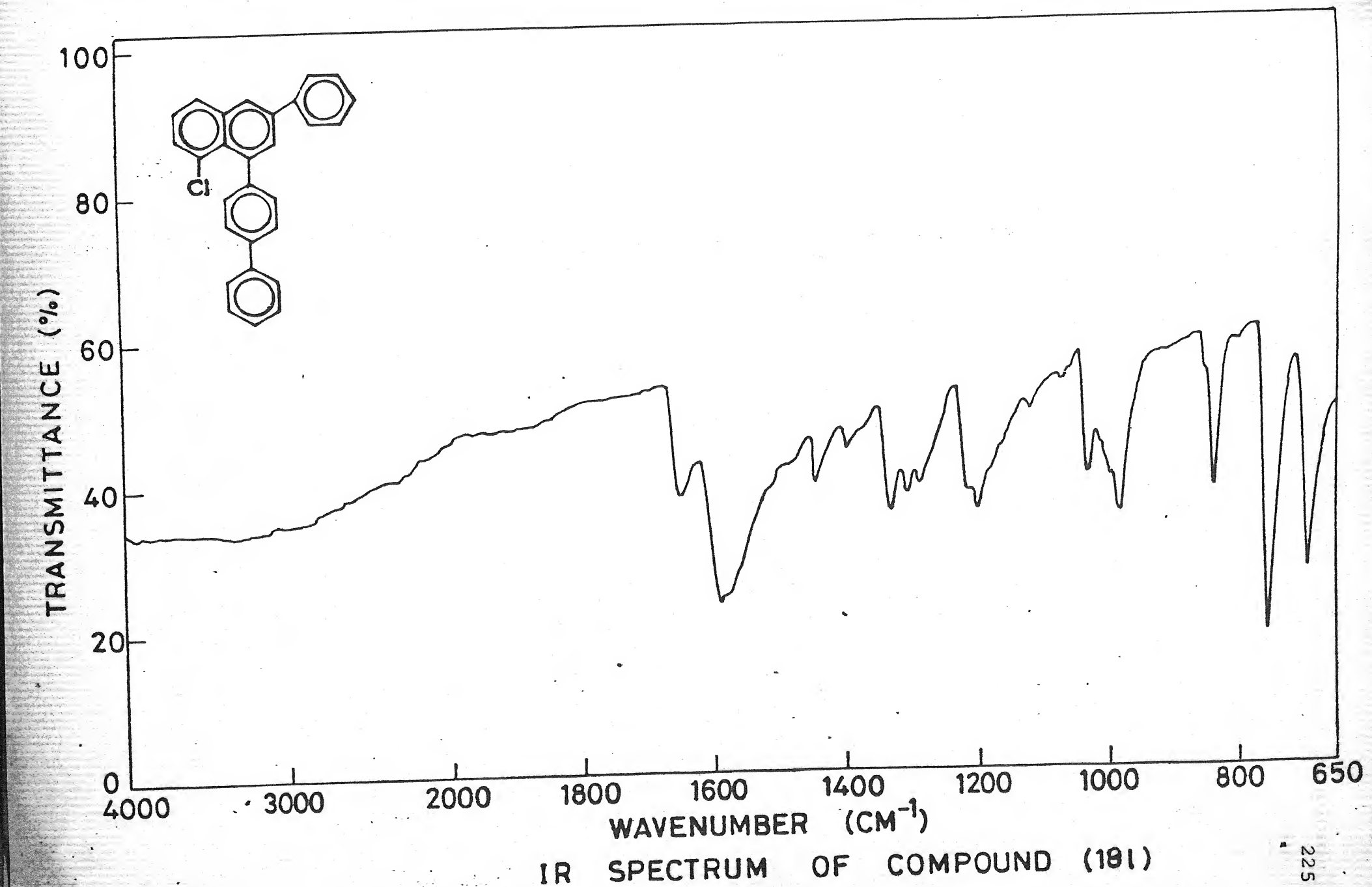
IR SPECTRUM OF COMPOUND (17 d)



IR SPECTRUM OF COMPOUND (17f)



NMR SPECTRUM OF COMPOUND (18d)



IR SPECTRUM OF COMPOUND (181)

i.e. BDH, S.Merck etc.. The starting materials were prepared according to references cited . Thus o-chlorobenzyl bromide [20] was prepared by the direct bromination of o-chlorotoluene at elevated temperature. Similarly benzyl bromide [21] was prepared from toluene.

The substituted benzylidene acetophenones, benzylidene 2-acetonaphthenes and benzylidene-2-acetothiophenes were prepared by a general procedure.[24] This method consists of stirring the equimolar quantities of aromatic aldehydes and methyl ketones in the presence of an alkali at 0°C . The resulting precipitate of α,β-unsaturated ketones was recrystallized from ethanol by benzene: pet ether (60 -80°C) in 40-80% yields.

VII.4.2 Preparation of benzylpyridinium bromide (14 a)

A solution of pyridine (50 mmole), benzyl bromide (50 mmole) in 50 ml of anhydrous benzene was refluxed on a water bath for 4 hrs. A solid mass was precipitated which was filtered, dried and recrystallized twice from chloroform-n-hexane to give white shining crystals of benzyl pyridinium bromide in 81% yield, m.p.-168-70°C (Lit. m.p.- 170-72°)[13].

Anal. data found : c, 56.58 ;H,4.90 %

Calcd. for ($C_{12}H_{12}BrN$) c,57.60 ; H,4.80 %

VII 4.3 Preparation of O- Chlorobenzylpyridinium bromide (14 b)

O- chlorobenzyl bromide (50 mmole) and pyridine (50 mmole) in anhydrous benzene (100 ml) was refluxed on a water bath

VII.4.5 Preparation of 1,3 diaryl-5-chloronaphalenes (18a-m)

A solution of o- chlorobenzylpyridinium bromide (9 mmole) in 15 ml. of glacial acetic acid containing 3 g. of anhydrous zinc chloride, was poured into a 100 ml. round bottom flask. The flask was equipped with a reflux condensor. The solution was stirred during heating on a magnetic stirrer. In this solution was added dropwise, a solution of α,β -unsaturated ketones (9 mmole) in glacial acetic acid (35 ml.). This mixture was stirred at 200°C for 6-8 hrs. under nitrogen atmosphere. The resulting solution was left to stand overnight at room temperature. Ice cold water (50 ml.) was added to it . The precipitated solid so obtained, was filtered off, dried and chromatographed over neutral alumina. Chloroform fraction on recrystallization from an appropriate solvent gave a fine crystalline solid due to formation of 1,3 diaryl-5-chloronaphthalenes (18 a-m).

All the substituted naphthalene derivatives (18 a-m) gave satisfactory elemenental analysis. Their physical properties are listed in Table VII.1. The NMR and IR datas of substituted naphthalene derivatives are tabled in Table VII.2.

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Table VII.1 Physical Properties of 1,3-diarylnaphthalenes (17a-i) and 1,3-diaryl-5-chloronaphthalenes (18a-m)

Compd.	X	R^1	R^2	Yield (%)	m.p. (°C)	rect. solt.	Analysis found/(cald)(%) C	H
1	2	3	4	5	6	7	8	9
17a	H	C_6H_5	C_6H_5	45	107-09 (109-10)[25]	A	94.12 (93.28)	5.78 (5.71)
b	H	C_6H_5	4-$CH_3OC_6H_4$	50	85-89	B	89.13 (89.03)	5.77 (5.80)
c	H	C_6H_5	3,4-$O_2CH_2C_6H_3$	58	90-92	A	84.83 (84.82)	5.29 (5.23)
d	H	4-$CH_3C_6H_4$	4-$CH_3OC_6H_4$	60	118-20	B	88.80 (88.88)	6.12 (6.17)
e	H	2-$C_{10}H_7$	C_6H_5	70	180-82	A	94.72 (94.83)	5.12 (5.17)
f	H	2-$C_{10}H_7$	4-ClC_6H_4	65	192-94	B	85.43 (85.59)	4.61 (4.66)
g	H	4-ClC_6H_4	4-$NO_2C_6H_4$	50	212-14	B	73.90 (73.99)	3.83 (3.89)
h	H	4-$C_6H_5C_6H_4$	C_6H_5	55	184-86	A	94.31 (94.38)	5.68 (5.62)

Table VII.1 (Contd.)

1	2	3	4	5	6	7	8	9
17i	H	2-$C_{10}H_7$	3-$CH_3C_6H_4$	50	92-94	B	94.11 (94.18)	5.86 (5.81)
18a	Cl	C_6H_5	C_6H_5	40	94-96	B	83.88 (83.94)	4.84 (4.77)
b	Cl	C_6H_5	4-$CH_3C_6H_4$	48	108-10	C	84.09 (84.02)	5.08 (5.14)
c	Cl	C_6H_5	4-$CH_3OC_6H_4$	56	125-27	A	80.21 (80.12)	4.81 (4.93)
d	Cl	C_6H_5	4-ClC_6H_4	58	110-12	C	75.59 (75.64)	4.09 (4.01)
e	Cl	C_6H_5	3,4-$O_2CH_2C_6H_3$	50	133-35	C	77.36 (77.42)	3.71 (3.65)
f	Cl	4-$CH_3C_6H_4$	C_6H_5	60	121-22	A	84.09 (84.02)	5.08 (5.14)
g	Cl	4-$CH_3C_6H_4$	4-$CH_3OC_6H_4$	54	95-97	B	80.27 (80.33)	5.38 (5.30)
h	Cl	4-ClC_6H_4	4-$NO_2C_6H_4$	50	190-91	B	69.92 (69.84)	3.51 (3.44)
i	Cl	2-$C_{10}H_7$	C_6H_5	65	170-72	C	85.53 (85.60)	4.58 (4.66)
j	Cl	2-$C_{10}H_7$	4-ClC_6H_4	60	171-74	A	78.29 (78.20)	4.10 (4.01)

Table VII.1 (Contd.)

1	2	3	4	5	6	7	8	9
18k	Cl	3-$C_{10}H_7$	3-$CH_3C_6H_4$	55	190-92	B	85.69	5.10
							(85.60)	(5.02)
l	Cl	4-$C_6H_5C_6H_4$	C_6H_5	55	160-64	C	86.11	4.79
							(86.04)	(4.87)
m	Cl	2-C_4H_3S	4-$CH_3OC_6H_4$	65	171-73	A	71.83	4.37
							(71.90)	(4.28)

A = Benzene/pet. ether

B = Chloroform /pet. ether

C = C_6H_6 : pet. ether

Table VII.2 Spectral Data of 1,3-diarylnaphthalenes (17 a-i) and 1,3-diaryl-5-chloronaphthalenes (18 a-m)

Comd.	IR DATA (KBr) Cm^{-1}			NMR ($CDCl_3$)		
	$\nu C=C$	$\phi C-H$	$\nu C-Cl$	δ(ppm)	No. of protons	Assignment
1	2	3	4	5	6	7
17a	1595	995	–	–	–	–
b	–	–	–	6.70-8.10,m	15 H	phenyl+naphthyl
				3.70,s	3 H	OCH_3
c	1600	990	–	6.80-8.00,m	14 H	phenyl+naphthyl
				6.00,s	2 H	OCH_2O
d	1600	1000	–	6.65-7.95,m	14 H	phenyl+naphtyl
				2.30,s	3 H	CH_3
				3.72,s	3 H	OCH_3
e	1590	980	–	–		
f	1595	997	–			
g	1600	998	–			
i				6.72-8.22,m	17 H	phenyl+naphth
				2.28,s	3 H	CH_3
18a	1590	985	780	6.95-8.21,m	14 H	phenyl+naphth
				2.48,s	3 H	CH_3

Table VII.2 (Contd.)

1	2	3	4	5	6	7
18c	1598	988	788	6.80-8.23,m	14 H	phenyl+naphth
				3.81,s	3 H	OCH_3
d	1608	990	782			
e	1600	990	790	6.70-8.10,m	13 H	phenyl+naphth
				6.09,s	2 H	O_2CH_2
g	1575	990	780	6.87-8.25,m	13 H	phenyl+naphth
				2.30,s	3 H	CH_3
				3,71,s	3 H	OCH_3
h	1608	994	790			
i	1612	990	800			
j	1612	998	802			
k	1600	985	795	6.85-8.35,m	16 H	phenyl+naphth
				2.31,s	3 H	CH_3
l	1600	995	770	6.80-8.20,m	12 H	thiophenyl
				3.85,s	3 H	phenyl+naphth

s = singlet

m = multiplet

ν = stretching vibration

φ = out of plane deformation of hydrogens attached to aromatic nucleus.

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